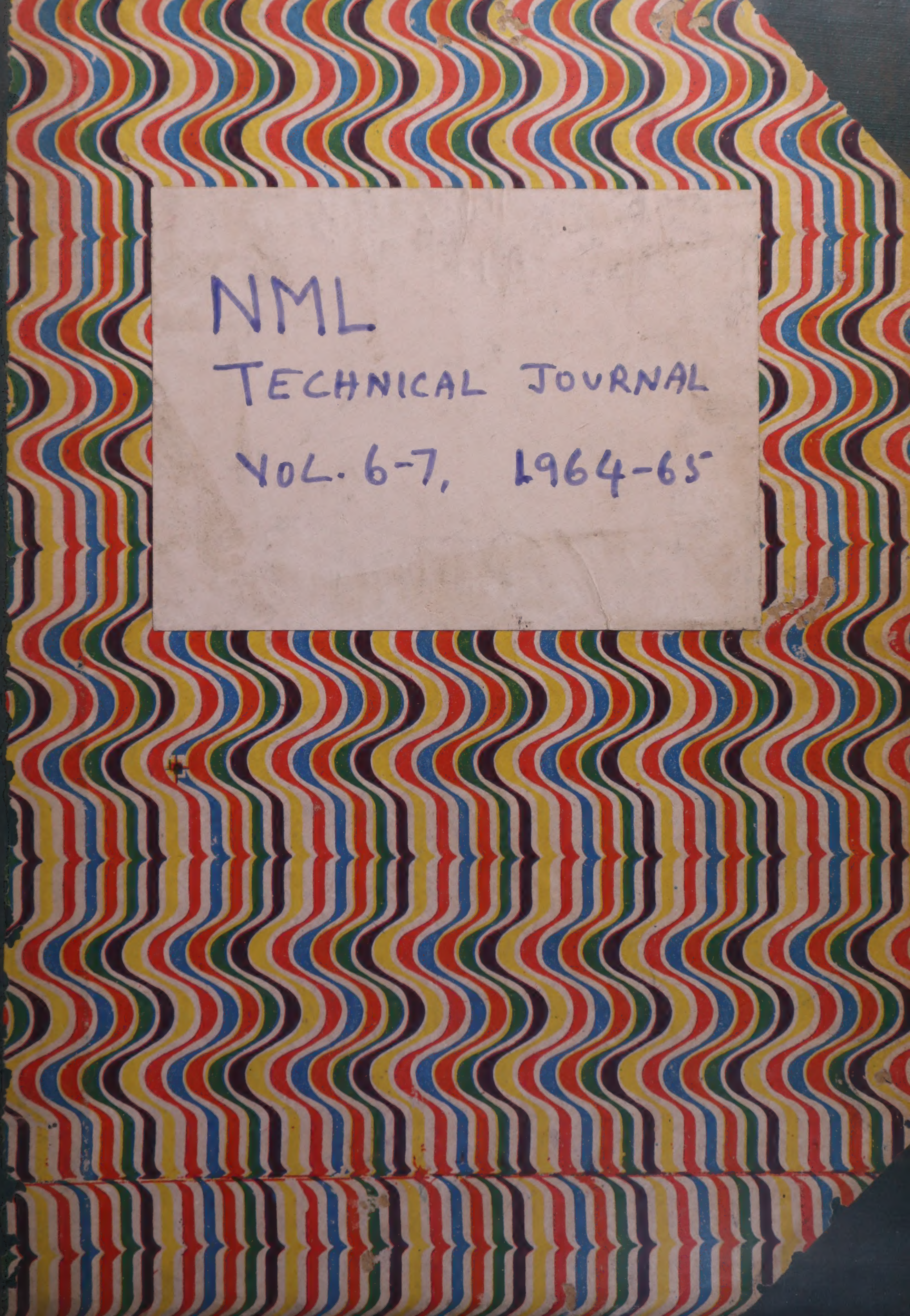

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VOL. 6-7, 1964-65

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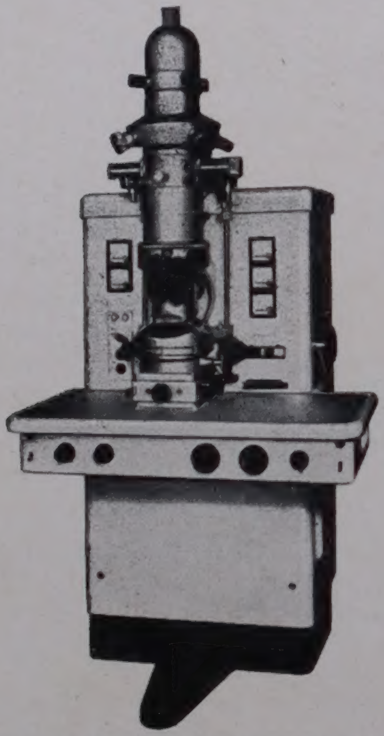
FEBRUARY 1964

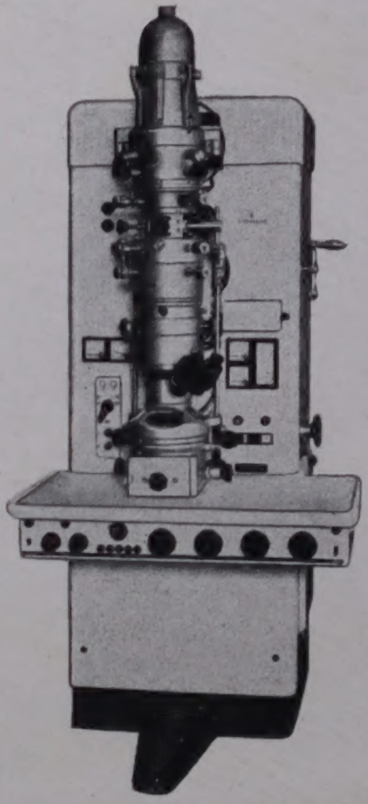
Vol. VI No. I

NATIONAL METALLURGICAL LABORATORY

Council of Scientific & Industrial Research

JAMSHEDPUR—INDIA





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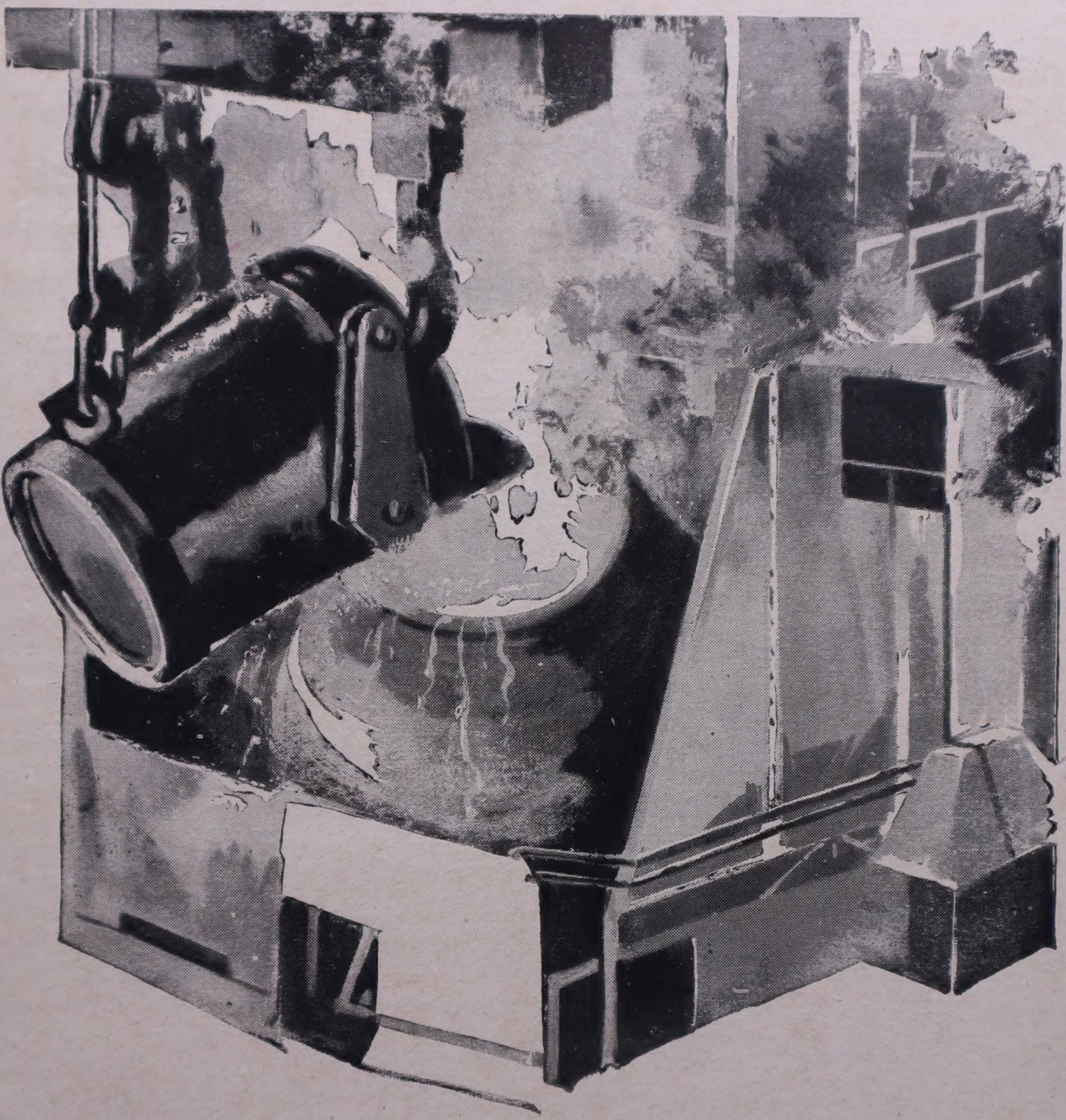

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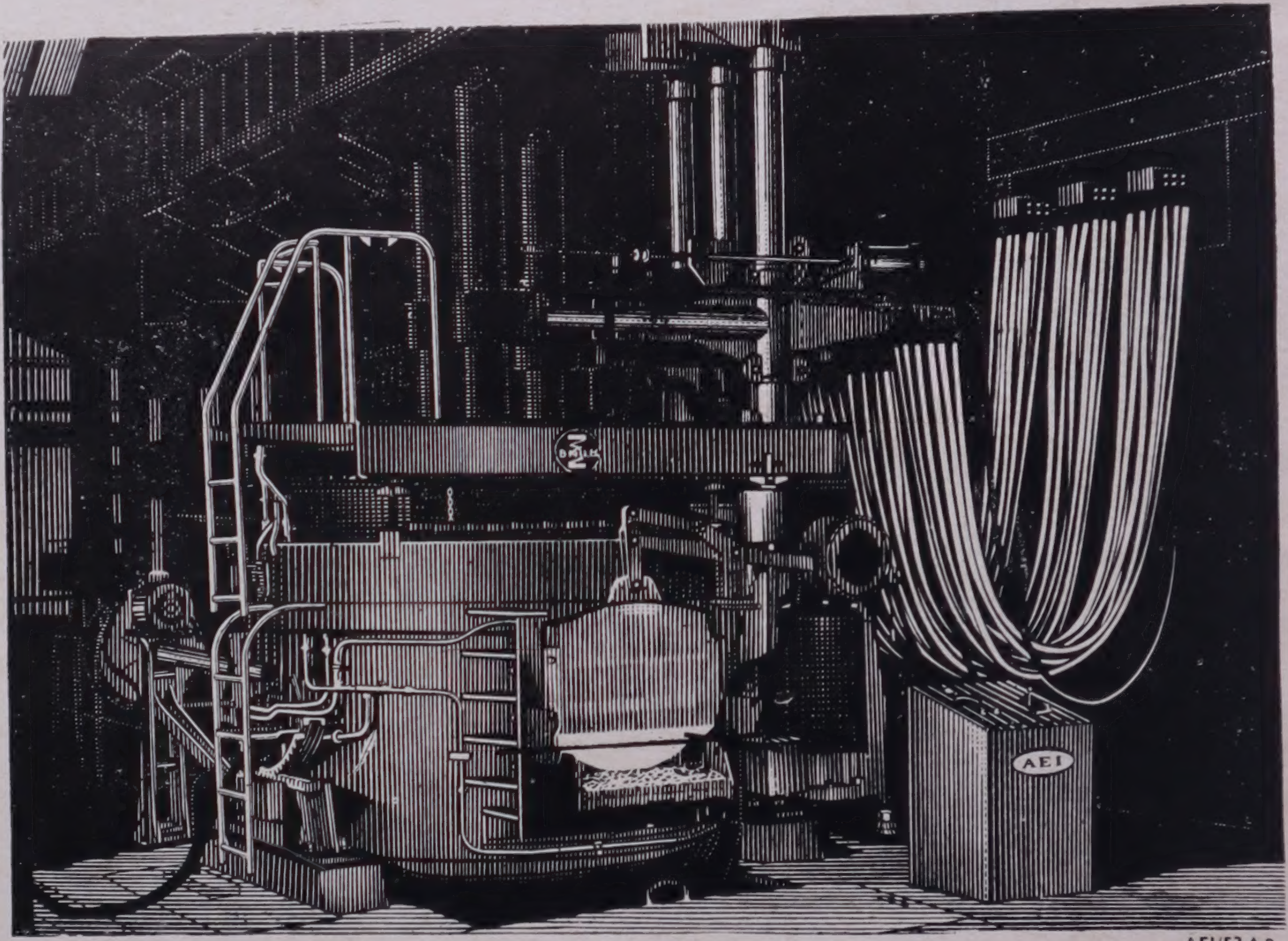

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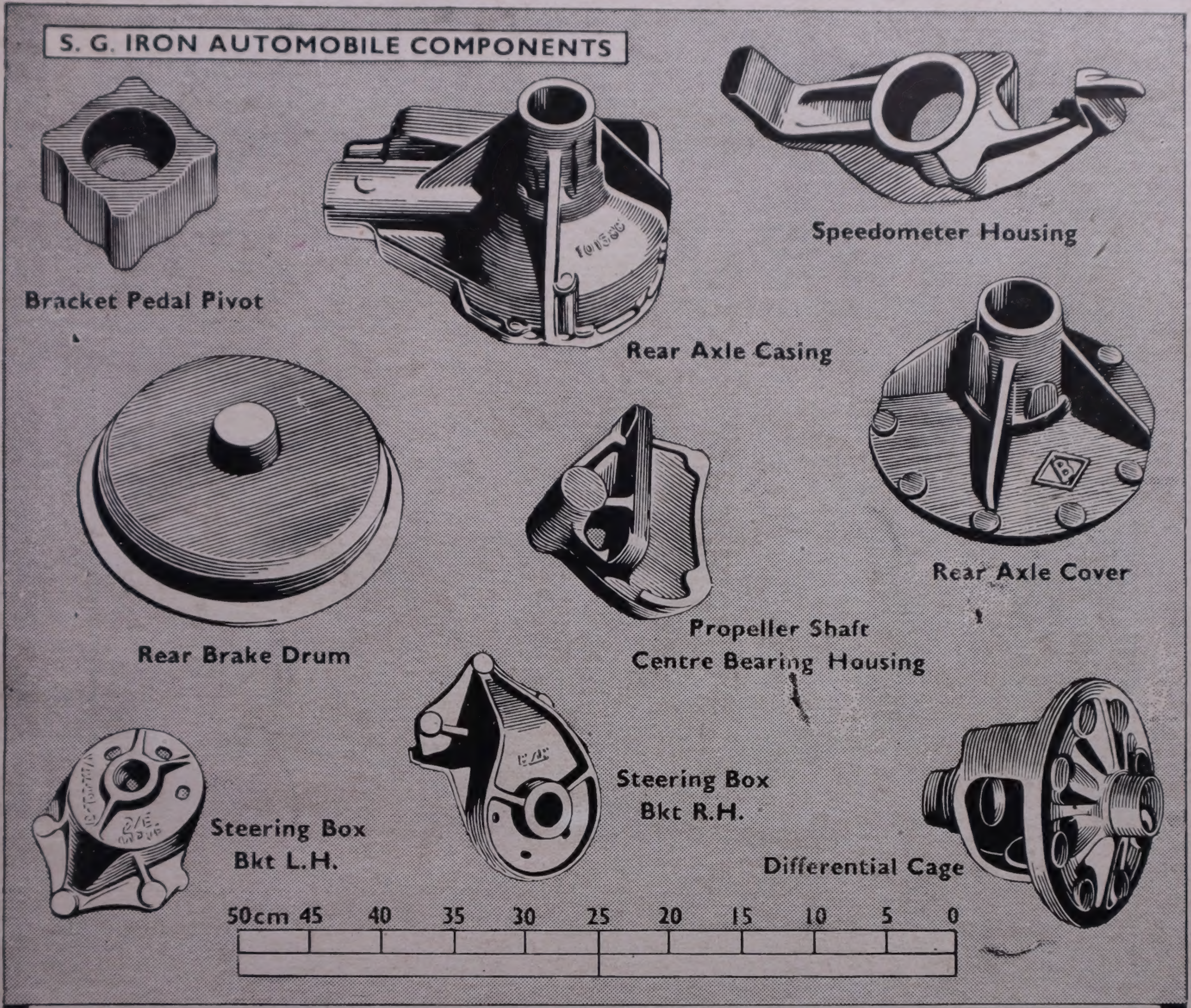
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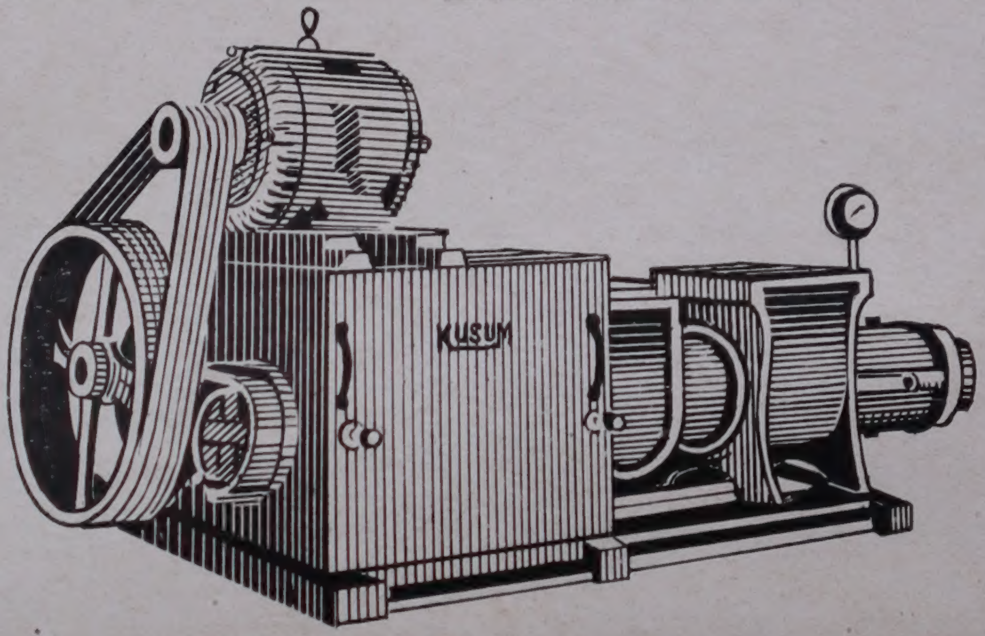

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VOLUME VI **NUMBER 1** **FEBRUARY 1964**

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Editor

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Kiheji Tamaki

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NML TECHNICAL JOURNAL

VOL. VI No. I FEBRUARY 1964

Symposium on Metallurgical Wastes

WHILST the smelting of ores has always received the metallurgical limelight, the utilization of metallurgical wastes has always been "back yard" in character and execution and yet basis of overall economics of metallurgical operations rests squarely on the latter. In holding possibly the first Symposium of its kind on the subject, the National Metallurgical Laboratory hopes to focus due attention of metallurgical "back room" boys on diverse aspects of the important subject of "Utilization of Metallurgical Wastes" particularly under Indian conditions of a fast developing economy. The subject is as vast as it is challenging. The technical and research papers to be presented at the Symposium and their discussion will no doubt stimulate original thought on diverse phases of the complex subject, opening fresh avenues and scope for maximum utilization of metallurgical wastes and by-products.

As in the past, we sincerely welcome all delegates and participants from home and overseas to the NML Symposium—we greatly appreciate their joining us and heartily wish them a thoroughly enjoyable visit to our country and of course, to the National Metallurgical Laboratory. This issue of NML Technical Journal presents the programme of the NML Symposium and abstracts of all the research and technical papers to be presented and discussed.

This year the NML Symposium is taking place in the warm Indian weather—no doubt the Symposium "by-products"—the professional ties and friendship would be equally warm and ever-basking.

SYMPOSIUM ON UTILIZATION OF METALLURGICAL WASTES

PROGRAMME

INAUGURAL SESSION

Tuesday, March 10, 1964

11.30 a.m. to 1.30 p.m.

11.30 a m.	GREETINGS	Dr B. R. NIJHAWAN, *Director,* *National Metallurgical Laboratory,* *Jamshedpur.*
11.40 a.m.	OPENING ADDRESS	Sir JEHANGIR GHANDY, Kt., C.I.E., *Chairman,* *Executive Council,* *National Metallurgical Laboratory,* *Jamshedpur.*
11.50 a m.	INAUGURAL ADDRESS	HON'BLE Prof. HUMAYUN KABIR, *Union Minister for Petroleum and Chemicals,* *Government of India,* *New Delhi.*
12.05 p.m.	GROUP PHOTOGRAPH	In front of the main building of the National Metallurgical Laboratory.
12.15 to 1.30 p.m.	VISIT ROUND THE NATIONAL METALLURGICAL LABORATORY	

10.00 to 11.15 a.m.	Registration of Delegates	NML Main Building.

TECHNICAL SESSIONS

Tuesday, March 10, 1964

Session I: Utilization of Raw Materials Wastes and By-products

3 p.m. to 5.15 p.m.

Chairman	Dr A. G. RAPER, *Metallurgical and Technical Manager,* *Davy and United Engineering Co. Ltd.,* *England.*
Recorder	Mr R. M. KRISHNAN, *Assistant Director,* *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

Titles	*Authors*
1. The Rational Utilization of Fine Ores from the Lorraine Iron Ore Deposit.	J. ASTIER, M. BOUCRAUT, F. CHAPOTOT and P. FOLIE, *Institut de Recherches de la Siderurgie Francaise,* *France.*
2. Utilization of Important Mining and Metallurgical Wastes Employing Mineral Beneficiation Techniques.	M. S. CHOPRA, G. P. MATHUR, and P. I. A. NARAYANAN, *National Metallurgical Laboratory,* *Jamshedpur.*
3. Utilization of Fine Grained Raw Materials by Briquetting for Smelting of Ferro-manganese.	Dr. A. B. CHATTERJEA, S. R. GHOSH and J. GOSWAMI, *National Metallurgical Laboratory,* *Jamshedpur.*
4. Utilization of Metallurgical Wastes in Ferro-manganese Industry.	C. R. COIL and A. SANGAMESWARA RAO, *Ferro-Alloys Corporation Ltd.,* *Shreeramnagar, Andhra Pradesh.*
5. Research and Development Work on the Utilization of Metallurgical Wastes at the National Metallurgical Laboratory.	Dr B. R. NIJHAWAN, *Director,* *National Metallurgical Laboratory,* *Jamshedpur.*

5.25 p.m. TEA

6.45 p.m. Indian Dance and Variety Entertainment Show at the NML Auditorium, organised by the NML Club (by invitation).

Wednesday, March 11, 1964

Session II : Utilization of Gases in Iron and Steel Production

9.30 a.m. to 1.00 p.m.

Chairman	Dr P. A. YOUNG, *Director of Research,* *Head Wrightson & Co. Ltd.,* *England.*
Recorder	Mr H. V. BHASKAR RAO, *Assistant Director,* *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

Titles	*Authors*
6. Recovery of Unburnt Gases from Oxygen Blown Converters.	Dr H. MALCOR, *Chairman, Cie. des Forges et Acieries de la Marine ;* *General Manager,* *Cie. des Ateliers et Forges de la Loire,* *and Hony. Chairman, IRSID, France.*
7. Energy Recovery from LD Converters—A Descriptive and Thermodynamic Comparison.	B. S. HOLMES, E. M. WOOLLEY and Dr P. A. YOUNG, *Head Wrightson and Co. Ltd.,* *England.*
8. The Recovery and Utilization of Waste Gases in Iron and Steelmaking.	J. L. HARRISON, *Manager, Iron and Steel Processes,* *British Oxygen Ltd,* *England.*
9. Recovery of Waste Gas from Oxygen Converter by the O.G. Process.	M. YUKAWA, Dr M. ICHINOE and Dr J. IMAI, *Yawata Iron and Steel Co. Ltd.,* *Japan.*
10. Utilization of Waste Heat and Gas in Small Integrated Iron and Steel Making Unit.	B. L. SEN and P. K. BOSE, *Indian Oxygen Ltd.,* *Calcutta.*
11. Nickel Recovery from Low Nickel-Copper Ores.	Dr S. C. SIRCAR and YA. YA. MIKHIN, *Indian Institute of Technology,* *Kharagpur.*
12. Chloride Volatilisation by Salt Roasting.	D. V. JACKSON, T. J. N. GRAINGER-ALLEN and R. G. WHITTEMORE, *Warren Spring Laboratory, D.S.I.R.,* *England.*

Break for lunch.

Wednesday, March 11, 1964

Session III : Utilization of By-products and Wastes in Iron and Steel Production

2.30 to 5.30 p.m.

Chairman	... ...	Dr H. MALCOR, *Chairman,* *Cie des Forges et Aciers de la Marine ;* *General Manager,* *Cie des Ateliers Forges de la Loire ;* *Hony. Chairman, IRSID,* *France.*
Recorder	... ...	Dr S. S. BHATNAGAR, *Assistant Director,* *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

	Titles	*Authors*
13.	**S. L. Direct Reduction Process and its Application for Indian High and Low-grade Ores Utilizing Non-coking Coals.**	Dr W. JANKE and L. R. CHOUDHARY, *Lurgi Gesellschaft fur Chemie und Huttenwesen mbH.,* *West Germany.*
14.	**Utilization of Coke Breeze for Production of Pig Iron in Small Scale.**	Dr A. B. CHATTERJEA, J. GOSWAMI, S. K. BISWAS, R. SANTOK SINGH and J. S. PADAN, *National Metallurgical Laboratory,* *Jamshedpur.*
15.	**The New Stora Process for Iron Making.**	A. N. WHITING and Dr. A. G. RAPER, *Davy and United Engineering Co. Ltd.,* *England.*
16.	**Possible Economies Which Could be Effected in the Recovery of Metallics from Steel Mill Wastes.**	Dr. WILLIAM T. HOGAN, *Professor of Economics and Director of Research,* *Fordham University,* *New York, U.S.A.*
17.	**Utilization of Metallurgical Wastes on the Indian Railways—Ferrous Metals.**	K. C. CHOUDHURI and P. K. MUNSHI, *Research Design and Standards Organisation, Ministry of Railways,* *Chittaranjan.*

5.40 p.m. TEA

Thursday, March 12, 1964

Session IV: Utilization of Metallurgical Slags, etc.

9.30 a.m. to 1.00 p.m.

Chairman ... ... Dr WILLIAM T. HOGAN,
Professor of Economics and Director of Research,
Fordham University, New York,
U.S.A.

Recorder ... ... Mr H. P. S. MURTHY,
Senior Scientific Officer,
National Metallurgical Laboratory,
Jamshedpur.

PAPERS

	Titles	*Authors*
18.	**Production of Cement from Blast Furnace Slags and Utilization of Fly Ashes by the Sintering Process.**	H. KLIER and L. R. CHOUDHARY, *Lurgi Gesellschaft fur Chemie und Huttenwesen mbH.,* *West Germany.*
19.	**Investigations on Granulated Low Shaft Furnace Slag for the Production of Slag Cements.**	B. N. SINGH, P. C. DEBNATH, Dr. B. C. KAR and Dr. B. R. NIJHAWAN, *National Metallurgical Laboratory,* *Jamshedpur.*
20.	**Tisco Blast Furnace By-products.**	B. P. SINGH and P. M. MEHTA, *The Tata Iron and Steel Co. Ltd.,* *Jamshedpur.*
21.	**Scope for Utilization of Slags and Related Wastes from Indian Iron and Steel Plants.**	NARINDER SINGH, K. N. SRIVASTAVA, R. M. KRISHNAN and Dr. B. R. NIJHAWAN, *National Metallurgical Laboratory.* *Jamshedpur.*
22.	**Utilization of Low Shaft Furnace Slag as Light Weight Aggregate for Insulation Concrete.**	NARINDER SINGH, K. N. SRIVASTAVA, R. M. KRISHNAN and Dr. B. R. NIJHAWAN, *National Metallurgical Laboratory,* *Jamshedpur.*
23.	**Utilization of the Indian Blast Furnace Slag.**	S. K. CHOPRA and C. A. TANEJA, *Central Building Research Institute,* *Roorkee.*
24.	**Utilization of Blast Furnace Slag in the Manufacture of Slag Wool and its Products.**	R. P. PUNJ, *Punj Sons Private Ltd.,* *Jamshedpur.*

Break for lunch.

Thursday, March 12, 1964

Session V : Utilization of Non-ferrous Scraps and Recovery of By-products

2.30 to 5.00 p.m.

Chairman	...	...	Mr D. V. JACKSON, *Senior Scientific Officer,* *Warren Spring Laboratory, D.S.I.R.,* *England.*
Recorder	...	...	Dr RAJENDRA KUMAR, *Assistant Director,* *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

Titles	*Authors*
25. Utilization of Metallurgical Wastes on the Indian Railways—Non-ferrous Metals.	K. C. CHOUDHURI and P. K. MUNSHI, *Research Design and Standards Organisation, Ministry of Railways,* *Chittaranjan.*
26. Utilization of Red Mud.	C. SANKARAN and P. P. BHATNAGAR, *National Metallurgical Laboratory,* *Jamshedpur.*
27. Production of Secondary Aluminium—A Review.	M. C. SEN and Dr. T. BANERJEE, *National Metallurgical Laboratory,* *Jamshedpur.*
28. Metallurgical Wastes from Aluminium Smelters.	K. K. CHERIAN, *Indian Aluminium Co. Ltd.,* *Alupuram, Kerala.*
29. Bayer Plant Liquors—A source for Vanadium.	Dr. N. VENKATARAMAN and Dr. M. S. THAKAR, *Indian Aluminium Co. Ltd.,* *Chotamuri, Ranchi.*
30. Short Rotary Furnace and its Application in the Treatment of Battery Scrap.	Dr. W. SCHWARTZ and W. HAASE, *Lurgi Gesellschaft fur Chemie, und Huttenwesen mbH.,* *West Germany.*
31. Recovery of Lead from Scrap.	K. ROYCHOWDHURY, *Works Manager, The Eyre Smelting (P) Ltd.,* *Calcutta.*

5.40 p.m. TEA

Friday, March 13, 1964

Session VI : Concluding Session—Utilization of Pickle Liquors and Miscellaneous Residues

9.30 a.m. to 1.00 p.m.

Chairman	Dr B. R. NIJHAWAN, *Director,* *National Metallurgical Laboratory,* *Jamshedpur.*
Recorder	Mr H. K. CHAKRABARTY, *Senior Scientific Officer,* *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

Titles	*Authors*
32. Recovery of Metallic Zinc from Galvanizers' Dross.	Dr. M. N. PARTHASARATHY and B. C. AGRAWAL, *Indian Lead/Zinc Information Centre,* *Calcutta.*
33. Recovery of Zinc from Scraps and Wastes.	B. C. MUKHERJEE, S. C. AUSH, M. C. SEN and Dr. T. BANERJEE, *National Metallurgical Laboratory, Jamshedpur.*
34. Pickle Liquor Regeneration by Vacuum Crystallization.	H. WELLING, *Lurgi Gesellschaft fur Warmetechnick mbH.,* *West Germany.*
35. New Method for Treatment of Waste Pickling Acid.	K. TAMAKI, *Fuji Iron and Steel Co. Ltd.,* *Japan.*
36. Method for Regeneration of Waste Pickle Liquors.	V. KRAMARSIC, F. STROJIN and Prof. Ing. CIRIL REKAR, *Metallurgical Institute, Ljubljana,* *Yugoslavia.*
37. Treatment and Recovery of By-products from Pickling Liquor Wastes.	Dr. G. K. SETH and Y. S. MURTY, *Central Public Health Engineering Research Institute,* *Hyderabad Zonal Centre, Hyderabad.*
CLOSING REMARKS	Dr. B. R. NIJHAWAN, *Director, National Metallurgical Laboratory,* *Jamshedpur.*

Break for lunch.

Friday, March 13, 1964

2.30 to 4.00 p.m.	*Visit to Low Shaft Furnace and Mineral Beneficiation Pilot Plants of the National Metallurgical Laboratory.
	*Buses will leave from the main building of the National Metallurgical Laboratory.
4.00 to 5.30 p.m.	Visit round the National Metallurgical Laboratory.
5.40 p.m.	TEA

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Sd/- R. M. Krishnan
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Dated 28th February, 1964.

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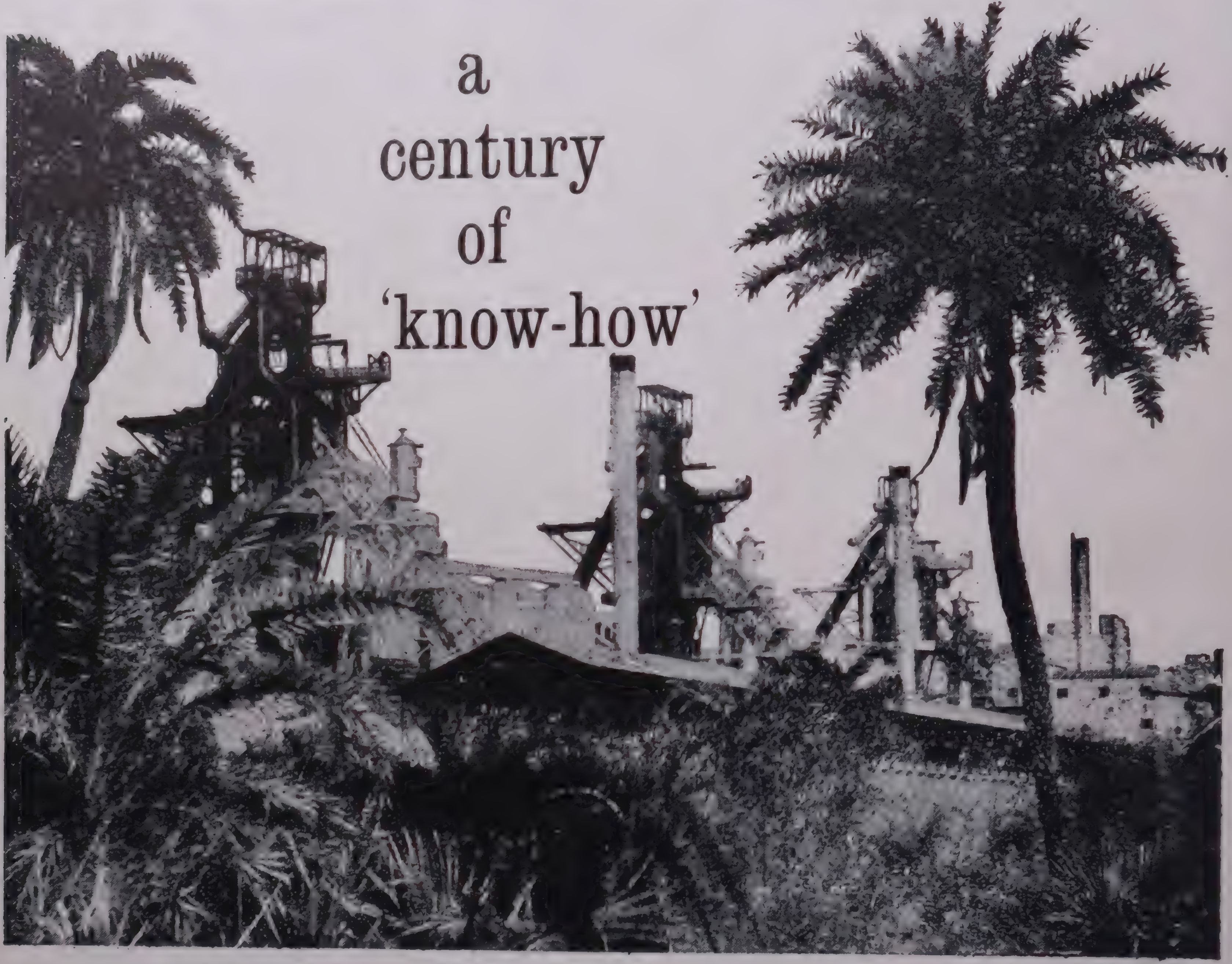

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Abstracts of Papers

Abstracts of papers—Symposium on Utilization of Metallurgical Wastes

1

The Rational Utilization of Fine Ores from the Lorraine Iron Ore Deposits

J. ASTIER, M. BOUCRAUT,
F. CHAPOTOT and P. FOLIE
IRSID, Maizieres-les-Metz Station, France.

MECHANIZATION of iron ore mines leads to a higher production of fines which have to be agglomerated before they can be charged into blast furnaces. In this paper the authors have examined the possibilities offered by the sintering and pelletizing processes towards a rational utilization of the Lorraine iron ore deposits. Sintering of fines from the low grade self-fluxing sedimentary Lorraine ores calls for better heat efficiency which has been discussed in detail both from theoretical and practical angles in relation to the main controlling parameters such as adjustment of bed depth ; double layer charging and use of preheated air or additional burners ; and selection of a suitable solid fuel. Industrial development of sinter in France and its use in the Lorraine blast furnaces have been fully described and illustrated. Investigations were also carried out recently on pelletizing of Lorraine iron ores, and the test data obtained from the IRSID Pelletizing pilot plant at Maizieres-les-Metz have shown that the pellets obtained possess good mechanical strength and chemical composition. A comparison between sinters and pellets is also given on basis of laboratory tests. In concluding, the authors stress that performances of blast furnaces with high sinter burden especially 100% self-fluxing sinter, are technically the best and can often suggest an economical scheme for crushing and grinding all the ore and as far as pelletizing is concerned it is pointed out that it might become necessary in the future to carefully compare it with sintering before making a final choice of process for agglomerating iron ores.

2

Utilization of Important Mining and Metallurgical Wastes Employing Mineral Beneficiation Techniques

M. S. CHOPRA, G. P. MATHUR and
P. I. A. NARAYANAN
National Metallurgical Laboratory, Jamshedpur.

THE application of beneficiation techniques for upgrading of low grade minerals and metallurgical by-products, has assumed importance not only because of the simplicity of the operation involved and the technical advancements in this field but also because of the economic advantages over most other methods. Though the amenability of the low grade ores to beneficiation has been established in most cases, studies on some of the metallurgical wastes have also proved equally successful.

During the past few years, exhaustive research investigation has been in progress at the National Metallurgical Laboratory for beneficiation of low grade manganese, chrome, iron ores, non-metallic minerals, etc. from various parts of India. Laboratory scale researches in some cases were sufficiently encouraging to justify large scale pilot plant studies at N.M.L. The results of these activities are briefly reviewed in the paper. Due to the expansion of the iron and steel industry in the country, it has become essential that iron ore fines amounting to 45% of the run-of-mine ore, and also large reserves of blue dust produced during mining operations should be efficiently utilized. Results of beneficiation of these fines have been very encouraging and the methods of their utilization after suitable agglomeration by sintering and pelletizing studies have been worked out.

Typical examples of recovery of metallics from drosses and slags and beneficiation of foundry sands, flue dust, rejects from beneficiation plants as well as from mines, are also presented. Wherever possible, the methods of beneficiation adopted and the important results obtained during laboratory and pilot plant studies have been presented. The use of beneficiation techniques is recommended for utilization of the mining and metallurgical wastes and consequent conservation of these resources wherever physical separation of the valuables is found feasible.

3

Utilization of Fine Grained Raw Materials by Briquetting for Smelting of Ferro-manganese

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FOR the utilization of large amounts of fine grained raw materials obtained during the smelting of ferro-manganese, investigations were conducted at the National Metallurgical Laboratory on making self-fluxing briquettes suitable for electro-thermal smelting employing various inorganic and organic binders. The physical characteristics such as shatter index, crushing strength and underload tests at elevated temperatures were conducted to assess the physical characteristics and furnace stability of the briquettes. Inorganic binders, such as bentonite and burnt lime proved to be unsatisfactory. Organic binders, such as molasses and sulphite lye conferred satisfactory physical properties particularly after heat hardening the briquettes at 200°C, but strength at elevated temperatures was inadequate for smelting purpose. As high temperature strength cannot be developed through the use of these binders, effects of addition of coking coal of various particle sizes were studied. The addition of 5 to 10% coking coal assured desired high temperature stability. The variation of grain size of coking coal did not cause any outstanding benefit. Briquettes containing 10% coking coal (–2·41 to 0·5 mm in size) with 4% sulphite lye revealed satisfactory characteristics for electro-thermal smelting.

4

Utilization of Metallurgical Wastes in Ferro-manganese Industry

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THERE are three main by-products, so far considered as wastes, from the ferro-manganese industry : slags containing 14–16% Mn, flue dust with 28–30% Mn and furnace gas containing 68–70% carbon monoxide.

About 150 000 tons of ferro-manganese is being produced in this country and it has been estimated that the manganese lost in the slag and flue dust would be sufficient, if recovered, to produce about 60 00 000 tons of steel. In view of the growing importance of manganese in ferrous and non-ferrous metallurgy, various possibilities of its conservation and recovery from such wastes are to be explored. Manganese can be conserved by (1) producing ferro-manganese by suitably adapted methods and (2) producing elecrolytic manganese.

Large quantities of gas amounting to about 750 to 850 Nm^3 per ton of alloy are now discharged into the atmosphere. These gases being rich in carbon monoxide and of high calorific value—2 200 K. Cals/m^3 or 250 B.T.U/ft^3—can be utilized as reducing agent, heating agent and for synthesis of methanol and chemicals.

5

Research and Development Work on the Utilization of Metallurgical Wastes at the National Metallurgical Laboratory

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THE science of metallurgy is based on extraction of metals from their ores on an economic basis. Whilst the metallic ores gradually become leaner, the requirements of different metals and their alloys on the other hand progressively become more specialised in terms of rigid service requirements in the background of rapidly expanding horizon of engineering technology.

The resulting spiralling production costs in their wake require the metallurgical 'back room' boys not only to improve the intrinsic economics of metal extraction and processing but also to devise economic means and develop technical 'know-how' for the recovery and utilization of most of the resulting by-products and metallurgical wastes. In these fields of turning metallurgical wastes into useful assets, metallurgical research ingenuity and engineering technology to-day present a broad spectrum as vast as it is challenging in the past background of general apathy and 'back-yard' treatment in making the best use of metallurgical by-products and wastes. Such a general situation is particularly pronounced and equally significant in India since optimum metallurgical techniques for recovery and utilisation of metallurgical wastes have to be basically indigenous in character and execution. In view thereof, metallurgical research and development work on this vitally important subject have to be well planned and systematically pursued. The National Metallurgical Laboratory realising the importance of the subject, started systematic studies on the recovery and utilisation of metallurgical wastes. In this paper, a review has been given of the research and development work undertaken in the National Metallurgical Laboratory on diverse phases of the subject whilst outlining fresh fields for work in these directions. References have been made in this paper to work done at the National Metallurgical Laboratory on the recovery of mine wastes in the form of low-grade ore discards such as that of the fines and their beneficiation and subsequent agglomeration through various means for optimum uses. Details have been furnished of extensive work undertaken on the treatments of different types of slags produced in the iron and steel industry, treatment of drosses, swarfs, skimmings and residues by pyro-, hydro- and electro-metallurgical techniques particularly in the case of non-ferrous metallic residues and by-products met with. Reference has been made to the rather unconventional approaches on the subject, such as the utilisation of granulated ground blast furnace slag for coal mine stowing in view of scanty reserves of silica sand for the purpose. Fundamental work on the subject, such as by hot stage microscopy relating to phase studies, has formed an important link of such investigations at the National Metallurgical Laboratory. Further plan of work in the background of current thinking on the subject has been referred to ; the scope for future work is vast indeed offering high premium to metallurgical research ingenuity both in planning and execution and in which the National Metallurgical Laboratory is to-day actively engaged upon.

6

Recovery of Unburnt Gases from Oxygen Blown Converters

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CHARACTERISTICS of the unburnt gases from oxygen blown converters have been examined, discussed and compared to show that their recovery is highly advantageous. Some difficulties are encountered in connecting the converter mouth to the recovery device. The tight connection system patented by the Cie. des Ateliers et Forges de la Loire (France) and the open connection method patented by the Institut de Recherches de la Siderurgie Francaise (France) have been described in detail and their performances discussed. On the basis of the experience gained and data collected from plant trials the author concludes that unburnt gases from oxygen blown converters can be safely recovered and cleaned and that recuperation of their latent heat will substantially increase the thermal efficiency of the steel process.

7

Energy Recovery from LD Converters—A Descriptive and Thermodynamic Comparison

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THE general problem of the utilization of waste gases from oxygen steelmaking processes is considered, and detailed descriptions are given of waste heat boilers and gas recovery plants for LD converters. The problem is then analysed in terms of both the first and second laws of thermodynamics.

8

The Recovery and Utilization of Waste Gases in Iron- and Steelmaking

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CLOSE economic and practical study of the recovery possibilities is essential to make the best use of the chemical and sensible heats arising from steelmaking processes. Though satisfactory means do exist to convert the energy to steam or to collect the gas and store it for a number of uses, it seems desirable that alternative methods be developed.

Suggestions have been put forward for using the energy to preheat scrap or to reduce fine ores. It may be possible to handle, in the pre-reducing cycle, the fine dust from the fume cleaning system. If processes are developed they should be capable of providing an end product comparable in price with alternative coolants for the LD process. The prices of such materials would vary according to availability. Therefore comparison cannot be made on a general basis, but must be individually investigated in a given locality.

9

Recovery of Waste Gas from Oxygen Converter by the O. G. Process

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EXTENSIVE studies carried out on the recovery of CO rich oxygen converter gas in the unburnt state and tests conducted over a period of about eighteen months, covering 220 heats, have shown that the oxygen converter gas recovery process can be safely adopted on an industrial scale and that the gas recovered will contain 70–90% CO. The Tobata No. 2 LD plant was fitted with O.G. process equipment and started operation in March, 1962. The present report gives an account of the tests, the compositions of the gas recovered and characteristics of the dust collected.

10

Utilization of Waste Heat and Gas in Small Integrated Iron- and Steelmaking Unit

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THE economics of a small scale iron- and steelmaking unit comprising low shaft furnaces and top or side blown oxygen steelmaking converters largely depend on the effective utilization of the waste heat gases. This paper examines the availability of waste gas from low shaft furnaces, LD converters, etc. and discusses its subsequent utilization.

If low shaft furnaces are to be set up in different regions of the country where non-coking coal, iron ore and limestone are abundantly available for steelmaking purposes, the economics of such units combined with oxygen steelmaking process cannot be satisfactorily balanced without a very effective use of waste heat and gas including their applications in other ancillary industries e.g. cement, fertilizer and chemicals based on steel plant by-products.

The availability of low cost oxygen and nitrogen from tonnage oxygen plant will play a significant role in the economics of such integrated projects.

11

Nickel Recovery from Low Nickel-Copper Ores

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THE possibility of nickel extraction from copper matte containing small amounts of nickel has been examined. It is shown that nickel can be extracted into slag phase by addition of flux at a predetermined time. By proper adjustment of the nickel rich slag addition and of the converter blow, a nickel rich copper matte can be obtained, which can be treated in the conventional way to give nickel metal. Also, the circulation of nickel between converter and reverberatory can be eliminated, thus achieving smoother operation of the reverberatory furnace.

12

Chloride Volatilization by Salt Roasting

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A STUDY of past work on chloride roasting and volatilization for recovery of non-ferrous metals suggests that attempts have been made to develop processes without first obtaining a full understanding of the reactions occurring and, in consequence, no volatilization process has had lasting economic success. This paper describes some preliminary experimental work designed to provide further information on the reaction processes. Results of chloride volatilization experiments using pure metal oxides, synthetic mixtures, pyrites cinders and samples of tin ore are given. The possibility suggested of treating pyrites cinders by firing pellets containing $CaCl_2$ on a sinter strand is considered and some results obtained on a small sinter pot are given. The collection of volatile chlorides is discussed.

13

SL Direct Reduction Process and its Application for Indian High and Low Grade Ores Utilizing Non-coking Coals

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STEEL works in India are at present concentrated around the deposits of rich ore and coking coal. With the projected development of steel and other industries, steel plants will have to be set up throughout the country including areas possessing only non-coking coals and inferior ores. Direct reduction processes would be of great interest in such cases. This paper describes the development of the SL direct reduction process and reports test results from a 1 ton/day unit and a semi-commercial plant of 100 ton/day capacity. The authors have discussed the flexibility of the process to suit the raw materials and end product requirements. Conversion of the reduced product into pig iron or steel has also been described together with the economic aspects of production.

14

Utilization of Coke-breeze for Production of Pig Iron on Small Scale

A. B. CHATTERJEA, J. GOSWAMI, S. K. BISWAS,
R. SANTOK SINGH, and J. S. PADAN

THE paper presents the results of research investigation on the utilization of coke breeze available from the integrated iron and steel plants for the production of pig iron on a small scale. Investigations were conducted on making self-fluxing briquettes containing iron ore fines, coke-breeze and limestone dust employing bentonite as a binder and smelting of the briquettes in a small blast furnace designed and fabricated at the National Metallurgical Laboratory. The effect of various binders on briquetting was studied ; bentonite was preferred in view of its low cost. The physical properties and high temperature stability of the briquettes were comprehensively studied. Smelting performance of the briquettes has been discussed on the basis of operational results obtained with the objective of utililizing abundance of coke-breeze currently surplus at the steel plants.

15

The New Stora Process for Ironmaking

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THE new Stora ironmaking process is described and compared with other ironmaking processes ; the process has several distinct advantages where, for example, there is a supply of high grade ore and a shortage of metallurgical coke.

A liquid product of controlled composition and temperature is produced. This provides an ideal feed material for oxygen steelmaking processes or foundry application.

Low phosphorus pig iron can be produced from high phosphorus ore when basic linings are used and little or no preparation of the fuel and ore is required prior to reduction.

Low grade carbonaceous fuels, such as coke-breeze and certain types of coal can be used, and the total fuel consumption is low.

Early indications are that for small scale operations, for example up to 150000 tons of pig iron a year, the process is cheaper both in capital and operating costs than other ironmaking processes.

16

Possible Economies which could be effected in the recovery of metallics from Steel Mill Wastes

WILLIAM T. HOGAN

Professor of Economics and Director of Research, Fordham University, New York, USA.

… … …

17

Utilization of Metallurgical Waste on the Indian Railways—Ferrous Metals

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THE authors have examined the situation of ferrous scrap in India and particularly with the Indian Railways. Different methods of use of ferrous scrap on Indian Railways have been reviewed with special emphasis on the utilization of cast iron swarfs by melting in cupola based on (*i*) Crofts method (*ii*) Briquetting of cast iron swarfs and (*iii*) Direct charging by Sandwich technique.

18

Production of Cement from Blast Furnace Slags and Utilization of Fly Ashes by the Sintering Process

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USE of blast furnace slags for the production of hydraulic binding agents is very common in European countries particularly in the Federal Republic of Germany. The paper discusses the chemical compositions of Indian blast furnace slags and their suitability for the production of binding agents. Manufacture of Portland cement clinker from blast furnace slags through sintering process and its further processing into Portland blast furnace cements and other Portland cements are described. The advantages of the sinter process have been explained on the background of a slag cement plant operating on this process since 1953. Fly ash from power plants can also be utilized after sintering, the fly ash clinker being used as raw material for the manufacture of various construction materials. Details of a plant engaged on such work since 1958 have been included in the paper.

19

Investigations on Granulated Low Shaft Furnace Slag for the Production of Slag Cements

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LATEST technical developments in diverse utilization of granulated blast furnace slag for the production of Portland slag cement have been reviewed in this paper including references to appropriate standard specifications in vogue in different countries including India. The chemical and physical requirements for the production of slag cement from blast furnace slag have been discussed in relation to the low shaft furnace slag produced in the pilot plant of the National Metallurgical Laboratory. The suitability of low shaft furnace slag for the production of slag cement has been discussed on the basis of experimental investigations and composite trials

based on different admixtures of the ground slag with Portland cement, etc. The investigation results have established that the low shaft furnace slag cement used with Portland cement as activators satisfies the requirements of A.S.T.M., B.S. Specifications and Indian Standards Specifications in relation to the requirements of chemical composition, compressive strength, tensile strength, setting time, soundness, sulphate resistance of the slag cement, etc. The hydraulicity of the ground slag was evaluated on the basis of its chemical composition in relation to different established formulae and relationships.

In the Pilot Low Shaft Furnace operating at the National Metallurgical Laboratory, the results presented on the utilization of low shaft furnace slag will no doubt find eventual industrial scale application when the growth of small foundry iron production plants in India projected during the Third and Fourth Five Year Plans is stepped up. Meanwhile, results of the low shaft furnace slag whilst conforming to the standard pattern of quality and accepted uses of blast furnace slag, are specifically those presented, it is believed, perhaps for the first time in technical literature.

20

TISCO Blast Furnace By-Products

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THE article discusses the optimum utilization of blast furnace by-products with particular reference to local conditions. The major by-products from the blast furnace are gas, slag and flue dust. Their utilization at the Jamshedpur works is described and suggestions are made for further development.

At Tisco, up to 97 per cent of the blast furnace gas is utilized and flue dust has been used in the sinter mix. About three hundred tonnes of slag are being granulated per day for the cement plant at Jhinkpani, and production of granulated slag can be stepped up if required. Indian blast furnace slag has a high alumina content and could be used in glass manufacture, as road ballast and as an aggregate for concrete while foamed slag may be suitable for making sound proof wall bricks. Flue dust and sludge which are not utilized in Tisco at present may be used with sinter mix in the future.

21

Scope for Utilization of Slags and Related Wastes from Indian Iron and Steel Plants

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K. N. SRIVASTAVA and B. R. NIJHAWAN
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RECOVERY and utilization of slags and related by-products in modern iron and steel industry present a vast scope and are challenging ingenuity in evolving applications other than those hitherto conventionally established—amongst the latter are the use of blast furnace slags for concrete aggregate, bituminous road aggregate, rail ballast, soil conditioners, slag wool, etc. Foamed blast furnace slag provides suitable aggregate for light weight concrete building material, possessing adequate thermal and accoustic insulation properties. Granulated blast furnace slag finds the well-established application of blast furnace slag cement and special mortar. Use of the basic steel slags for fertilizers finds a world-wide application—the subject of basic steel slag has been discussed in this paper in relation to Indian steel slags in the context of potential indigenous applications. Recovery of metallic values from basic steel slag recycling in steel melting furnaces is today well established both in India and abroad. Soviet developments in this field include the treatment of molten steel slag with mineral additives for recovery of metallic values and conventional uses.

The paper also refers to the utilization of other by-products met with in mechanized iron ore mining, such as the blue dust, the ore fines in relation to potential uses in production of pure iron powder and agglomerated products such as pellets, sinter and briquettes for iron smelting. Various aspects of the subject have been critically reviewed in the background of introducing potential recovery cycles within the indigenous iron and steel industry on the basis of research and development work at the National Metallurgical Laboratory in close co-ordination with the Indian steel plants.

22

Utilization of Low Shaft Furnace Slag as Light Weight Aggregate for Insulation Concrete

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MOLTEN blast furnace slags containing low MnO and FeO and high sulphur contents when foamed whilst at high temperature with a limited quantity of water yield a porous, light and strong product which after crushing and grading, is suitable as coarse and fine aggregate for light weight concrete.

The authors have critically reviewed latest developments in the foaming processes whilst presenting their research results on the production of light weight insulation concrete from slags produced at the low shaft furnace pilot plant of the National Metallurgical Laboratory. The physical properities of the slag aggregate conformed to ASTM Specifications. Concrete mixes investigated on volume as well as on weight basis gave satisfactory unit weight, compressive strength and thermal conductivity values. Concrete with less or 'no fine' aggregate gave lower thermal conductivity value, low unit weight and low compressive strength whilst mixes with more fines possessed superior thermal conductivity, greater unit weight and higher compressive strength. In all cases, thermal conductivity value was below 2·0 Btu/(hr) (sq ft) (F°) (in.). The light weight concrete was about 60% lighter than gravel-sand concrete. Thermal conductivity values obtained at different temperatures by Blakeley and Cobb apparatus showed a steep rise with increase of the mean temperature.

On the basis of the research results, extensive use of slag in foamed form as aggregate for light weight concrete has been advocated.

23

Utilization of the Indian Blast Furnace Slag

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THIS paper deals with the current researches and some of the long term studies on the use of blast furnace slag in the building industry. The mineralogy of the air-cooled slag from the Tisco, Durgapur, Bhilai, Rourkela and Bhadravati steel plants has been reported. The more common minerals are melilite, oldhamite and pseudo-wollastonite while spinel or a combination of wollastonite and diopside has also been observed. No dicalcium silicate was observed. Glass was present in varying amounts. Hydraulicity and activation of the Indian slags which are characterised by relatively low lime and high alumina contents have been discussed. Optimum compositions for the manufacture of different types of slag cements have been reported and current studies on the utilization of Rourkela slag (2 to 4% Mn_2O_3 content) in the manufacture of Portland blast furnace cement have been described. Long term studies now in progress on the hydration, stability and durability of different types of slag cements are briefly reported and some problems in the field of slag utilization have also been mentioned.

24

Utilization of Blast Furnace Slag in the Manufacture of Slagwool and its Products

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Jamshedpur.

THE total demand of slag wool in India is 12 000 tons per annum by end of 1964 to meet the requirements of slagwool for insulation and other purposes. The paper describes the salient features of the processes employed for the manufacture of slagwool, namely, high pressure steam or air blown through the molten stream with the help of a single nozzle ; high pressure steam or air blown through equally divided streams with the help of a multiple nozzle unit ; single disc centrifugal process ; 3, 4 and 5 wheel centrifugal process; 'Super Tel' process in which the combination of spinning and blowing with high pressure hot gases is used. The properities of various types of slagwool manufactured have been compared and the quality control techniques employed during production have also been dealt with. The future requirements of slagwool in India for Fourth Five Year Plan have also been estimated.

25

Utilization of Metallurgical Wastes on the Indian Railways—Non-ferrous Metals

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THE paper is devoted to non-ferrous scrap and the scope for its utilization. The annual requirement of different non-ferrous virgin metals on Indian Railways and the types of scrap available have been reviewed and various methods of reclamation outlined, particularly the (i) Sigma Oil Method (ii) Bradley Process and (iii) Differential Melting Process for separation of bronze borings mixed with white metal and reclamation of scrap lead battery plates.

26

Utilization of Red Mud

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LARGE quantities of red mud are currently dumped to waste at aluminium production plants in India ; in some of the aluminium plants, 0·25 to 0·3 ton of red mud is produced per ton of bauxite treated. The recovery of aluminium, titanium, iron and vanadium oxides as by-products from this easily friable, finely divided red mud would greatly improve the overall economics of aluminium production. A review has been given in the paper of various processes for recovering the iron, aluminium, titanium and vanadium oxides from the red mud in the background of researches carried out at the National Metallurgical Laboratory on the recovery of alumina. The results of investigations on the recovery of alumina values from a red mud sample containing 21·4% Al_2O_3, 48% SiO_2, 20·8% Fe_2O_3, 28·8% TiO_2 and 1·8% CaO by soda ash and limestone roasting, have been reported. Various operating factors investigated included the effect of soda ash and lime on alumina recovery, temperature and time of roasting, leaching temperature and time, etc. The possibilities of utilizing the residue to produce pig iron and titania-rich slag or the ferro-titanium have been discussed.

27

Production of Secondary Aluminium—A Review

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IN this paper, the importance and feasibility of production of secondary aluminium and its alloys in India have been outlined. In the paper different kinds of scraps and wastes are enumerated of aluminium and its alloys and their quality and character. Various modes of utilization and methods of treatment, depending on the nature and composition of scraps, for the production of secondary aluminium and its alloys have been discussed at length.

28

Metallurgical Wastes from Aluminium Smelters

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THIS paper gives an account of the loss of aluminium metal in the dross, skimmings and sawings of casting units and loss of electrolyte materials in the reduction cell linings and exhaust gases of aluminium smelters. Methods adopted for recovery of the same are also dealt with briefly.

29

Bayer Plant Liquors—A Source for Vanadium

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VANADIUM is widely used in the production of various alloy steels and its compounds are employed in increasing quantities in different industrial oxidation processes. The authors have examined the possibilities of isolating vanadium salts from the Bayer Plant liquors where they find their way as an undesirable impurity while processing bauxite for the production of alumina. Chemical composition of the vanadium salts which can thus be separated has been studied and pilot plant data relating to the optimum operational conditions have been presented. A process is also described for the recovery of soda from this salt and elimination of a vanadium rich sludge. As vanadium is not so far industrially produced in the country, its tonnage requirement and available resources have been examined. A brief discussion is presented on Bayer Plant 'red mud' as a potential source of vanadium.

30

Short Rotary Furnace and its Application in the Treatment of Battery Scrap

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TREATMENT of battery scrap will gain more and more importance with advances in automation and increase in transport facilities. The short rotary furnace is eminently suited to the treatment of battery scrap by its capacity to quickly heat the charge at a low fuel consumption. It can easily convert battery scrap into antimonial lead producing a slag of low lead content. Coal being used as the reductant, soda ash, pyrite cinder or iron ore are suitable for fluxing. High smelting capacities and antimonial lead recovery are achieved under low flux consumptions.

31

Recovery of Lead from Scrap

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REVIEWING the current lead production, consumption and import figures, the author has shown the importance of recovery of lead and its alloys from scrap. The various sources of lead scrap and its forms have been discussed. Methods of recovery are outlined and utilization of the recovered metal described.

32

Recovery of Metallic Zinc from Galvanisers' Dross

M. N. PARTHASARATHI and B. C. AGRAWAL
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A CERTAIN amount of dross is inevitable even with the best galvanizing practice. The paper discusses the various sources of dross and the methods by which it can be kept to a minimum. The authors have also critically reviewed the well known processes of recovery of zinc from dross and discussed their economics with particular reference to Indian conditions.

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Recovery of Zinc from Scraps and Wastes

B. C. MUKHERJEE, S. C. AUSH, M. C. SEN and T. BANERJEE
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THIS paper consists of two parts. In the first part different types of scrap and wastes have been enumerated and their modes of production, composition, etc. have been discussed. Various methods of treatment of the scraps and wastes for the recovery of zinc and/or zinc compounds (especially oxide) have been reviewed. In the second part, results of some investigations carried out at the National Metallurgical Laboratory for the recovery of zinc and zinc oxide from a sample of treated zinc ash, have been presented.

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Pickle Liquor Regeneration by Vacuum Crystallization

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PICKLE liquor treatment involves the separation from the spent liquor of the ferrous sulphate formed during the pickling operation and the regeneration of the liquor by addition of concentrated sulpuric acid.

The liquor may be subjected to either concentration at high temperature so that ferrous sulphate precipitates in the form of mono-hydrate, or low temperature cooling whereby ferrous sulphate crystallizes out in the form of hepta hydrate. Advantages and disadvantages of different treatments have been examined in the paper.

The LURGI process based on low temperature cooling under vacuum has so far proved the most efficient. The process is continuous; it lends itself to both very small and very large pickling capacities and even permits treatment of bath liquor of low iron content. For an iron content of 60–70 grammes per litre of spent liquor, that of the treated liquor is as low as 20–30 gm, per litre with H_2SO_4 up to 28%. During the entire pickling process an almost constant Fe concentration is maintained in the pickle liquor, with maximum H_2SO_4 content which results in a higher pickling rate, and uniform surface quality of the pickled material. The author finally suggests uses for the hepta hydrate and gives the complete description of a process for decomposition of ferrous sulphate in the turbulent layer furnace together with a study of the economics of the process.

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New Method for Treatment of Waste Pickling Acid

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ABOUT 55 000 tons of cold rolled steel sheet are produced every month at the Hirohata Works of Fuji Iron & Steel Co. Before cold rolling the hot-rolled coils are subjected to sulphuric acid pickling entailing 4 500 to 6 000 m³ of waste pickling acid per month. In an attempt to utilize the sulphuric acid contained in the waste pickling acid, a new process of manufacturing iron oxide and ammonium sulphide has been developed, based on the Ishihara Oxidation Method, wherein ferrous sulphide in the waste acid is combined with ammonia and air to produce magnetite with slight absorption of water. This magnetite is precipitated and filtered and its ammonium sulphite is thus recovered. Our process is a modification of the above and is characterised by the following distinct features: the waste acid is neutralized with ammonia contained in the coke oven gas; the ammonium sulphide produced has equally good size distribution and colour as synthetic ammonium sulphide and iron oxide is also recovered.

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Method for Regeneration of Waste Pickle Liquors

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THE Metallurgical Institute in Ljubljana has developed a method for regeneration of ferrous sulphate pickle liquor. In this process a cavitation stirrer is used, which by oxidizing ferro-hydroxide makes possible the production of mineral pigments of various shades or of magnetite. It is possible to reduce this magnetite and use it very successfully in the powder metallurgy.

If the ferrous sulphate is neutralized and precipitated by means of the sodium brine, the sodium sulphate obtained can be dissolved by the electrolysis developed particularly for this purpose by Messrs E. Merck to recover a 50 per cent solution of sodium hydroxide which can be used again. The anode solution contains the sulphuric acid and the sodium sulphate yet undissolved. By under-cooling this solution a crystalline sodium sulphate decahydrate can be recovered to be returned into the electrolysis. The sulphuric acid solution combined with sulphuric acid being a residue after the

ferrous sulphate has been precipitated forms a sulphuric acid solution of suitable concentration to be used again for pickling.

This process is represented in a diagram, divided into nine phases and calculated for pickling 1 250 tons of hot rolled strips in 24 hours. By pickling, the surfaces of these strips are to be freed from 8·75 tons of scale considered mainly to be FeO. A material balance has been worked out for each of these phases, as well as for the complete regenerating process.

The method has been experimented on a semi-industrial plant, in its individual phases and as a whole. The capacity of the plant has been determined according to the prototype electrolysis of the sodium sulphate having a capacity of 1 500 amperes.

The authors finally give an estimation of costs per ton of pickled hot rolled strips, which shows that this regeneration method, though expensive—Rs 1·6 or more per ton of pickled strips—can be profitable under special circumstances.

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Treatment and Recovery of By-Products from Pickling Liquor Wastes

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Central Public Health Engineering Research Institute—Hyderabad Zonal Centre, Hyderabad.

THE paper discusses the process of pickling in the steel industry and gives the composition of the liquid wastes coming out of the pickling baths. The pollutional effects of these wastes when discharged on land or water environment and their toxicity to fish and other organisms have been mentioned. Methods of treatment and recovery of useful by-products from these wastes have been discussed with reference to :

(1) Dilution and disposal in the sewer or nearby stream provided the wastes get amply diluted.
(2) Neutralization with lime and recovery of ferrous sulphate and sulphuric acid or sulphonic acid and hydrated ferrous sulphate. Utilization of waste materials from other industries especially lime sludge from acetylene manufacture and water softening plants for neutralization purpose has also been indicated.
(3) Crystallization by evaporation and recovery of ferrous sulphate and sulphuric acid.
(4) Production of 'Ferron'—a constructional material.
(5) Recovery of electrolytic iron and regeneration of sulphuric acid by electrolysis.

The economics of neutralization with lime and recovery of ferrous sulphate and sulphuric acid which appears to be most suitable under Indian conditions have been detailed.

Recovery of Unburnt Gases from Oxygen Blown Converters

H. Malcor

PRODUCTION of oxygen blown steel has sharply increased in recent years mainly due to the LD process—used for hematite iron—and its derivatives the OLP, LDAC, LDP processes applied to high phosphorous pig iron and also the Kaldo and Rotor processes. Fig. 1 shows the increase in the world production of steel by oxygen processes.

One of the advantages of blowing pure oxygen is the elimination of nitrogen the presence of which is characteristic of the Bessemer and Thomas processes which yield a steel of excessive nitrogen content and are unsuitable for certain applications, such as sheets for deep drawing. On the other hand nitrogen carries away a considerable amount of heat : about 100 000 calories per ton of pig iron can be saved by using pure oxygen and may be utilized in the converter, for example to melt a considerable extra quantity of scraps (about 350 kg per ton of pig iron).

Furthermore, in the absence of nitrogen the gas leaving the converter contains 75 to 95% carbon monoxide and has a high calorific value of the order of 2 200 to 3 800 calories per normal cubic meter, which is twice or three times the calorific value of blast furnace gas; this gas is far more valuable than the Thomas converter gas with an average calorific value of 6 to 700 calories per normal cubic meter and even less at the end of the blow.

Treatment of one ton of hematite pig iron requires about 52 normal cubic meters of oxygen—of which about 40 are needed to burn the carbon, mainly into carbon monoxide—and produces about 72 normal cubic meters of carbon monoxide, the combustion of the latter yielding about 150 000 calories. This amount of heat is far from negligible when compared to the 1 000 000 calories per ton of pig iron available from a modern blast furnace gas after deducting the quantity required for blast compression and for the stoves. Another advantage in blowing pure oxygen is that the gas output from the converter is decreased to one third which considerably simplifies the recovery problems.

Recovery of unburnt gases

Recovery of unburnt gases further reduces the volume to be cleaned. In fact, combustion at the mouth of the converter not only requires the supply of air needed for combustion—2·4 cubic meters per cubic meter of carbon monoxide or 170 normal cubic meters per ton of pig iron—but also an excess of air for lowering the fume temperature prior to their entry into the heat exchanger (hood, water jacket, boiler, etc.).

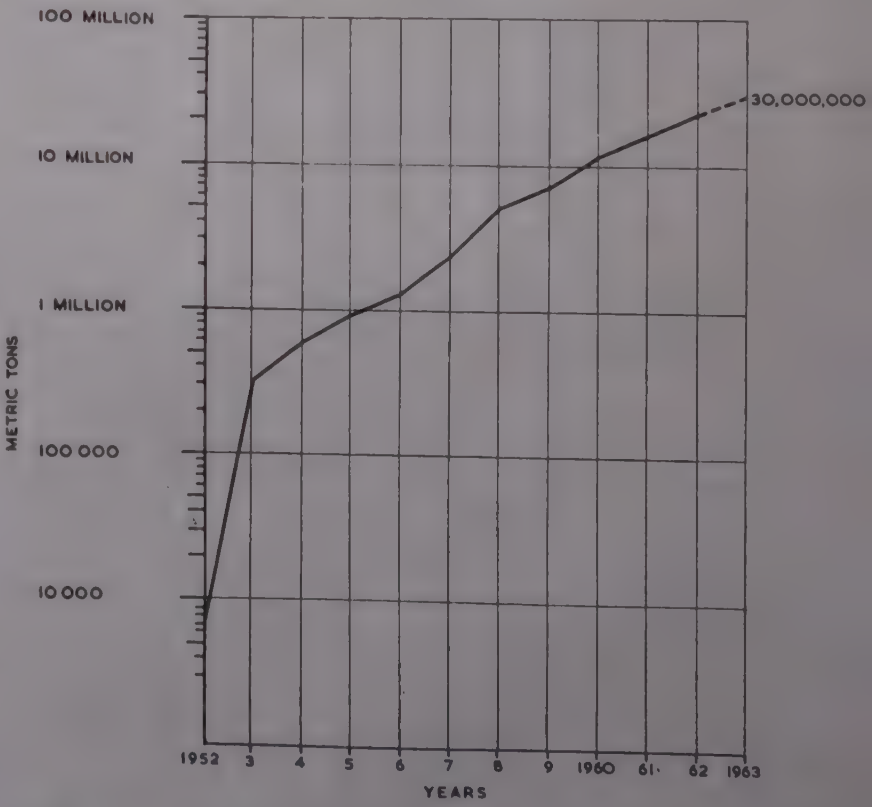
If for example the objective is an average temperature of 1 500°C for the fumes entering the hood, the volumes of fumes per ton of pig iron would be :

- 700 normal cubic meters for the Thomas process in the (hypothetical) case of recovery after combustion,
- 468 normal cubic meters for the LD—OLP process, with recovery after combustion, and
- 72 normal cubic meters only for the LD—OLP converter with recovery without combustion.

The above figures being in normal cubic meters the actual volumes would be 6·5 times greater, as the gases are to be recovered at a temperature of 1 500°C in all three cases which shows that the volumetric output of gas is enormous indeed.

It is interesting to note that the ratio between the first two cases is not even 2 : 1 ; this is because a large amount of excess air is required—300 cubic meters per ton of pig iron, in both cases—to burn the carbon monoxide and cool down the fumes to 1 500°C.

The volume of fumes to be recovered from the LD—OLP converter if combustion were reduced to nil, is 6·5 times lower than in the case of complete combustion



1 *World yearly output of oxygen blown steel*

Dr H. Malcor—Chairman, Cie. des Forges et Acieries de la Marine, Firminy, Saint-Etienne, General Manager, Cie des Ateliers et Forges de la Loire and Hony. Chairman, IRSID, France.

and cooling of the fumes to 1 500°C by excess air. It is only one tenth of that of Thomas converters.

Obviously, when the gases are completely burnt there is no limit to their dilution by excess air and the entrance temperature may be very low which however implies a large increase of the volume to be cleaned. Recovery of unburnt gases, on the other hand, necessarily results in an entrance temperature approximately equal to that of the steel in the converter.

The saving obtained by reducing gas outputs from 6·5 to 1 is important, partly because investment costs are much lowered—not only those directly connected with the fumes circuit (heat exchanger and dust removal) but also those related to the structure of the steel plant; the hood can be built lighter and stresses on the framework are reduced. In addition, the height of the steel plant can often be decreased. One last advantage in recovering unburnt gases is that the dust they carry does not get oxidized and remains mainly metallic and experience shows that it is then much easier to separate it.

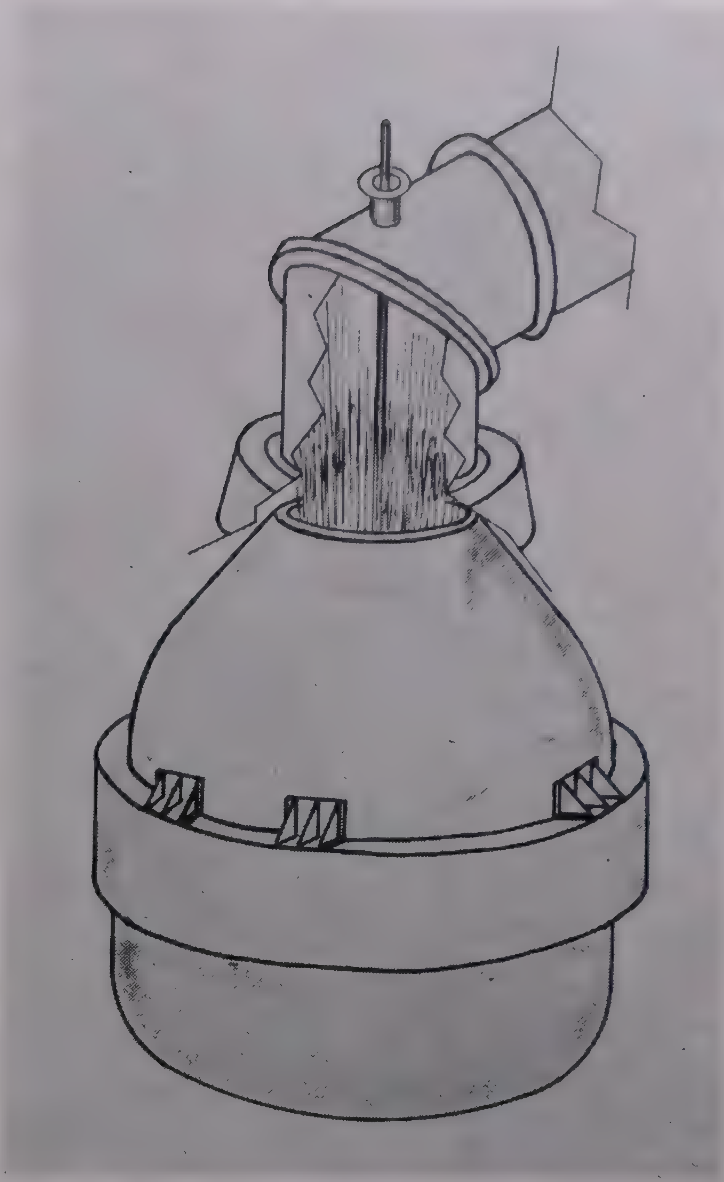
These considerations tend to prove that recovery of unburnt gases is a most attractive proposition. However, steel makers were reluctant for quite some time to take any step in this direction because they were rather skeptic about the practical realisation of the scheme.

There are two sources of difficulties. On one hand, the blowing operation is not a continuous process; at the end of the blow, when carbon combustion is nearly ended, not much gas and still less carbon monoxide leave the converter. The space through which the recovered gas passes cannot be permanently filled by a gaseous stream; interruptions in the arrival of the combustible gas should be taken care of. It would be too dangerous to leave these spaces filled with stagnant combustible gas; air would inevitably enter and cause explosions. It is therefore essential to provide for the purging of the exchanger and dust catcher at the end of each blow. This raised some doubts, although every open hearth furnace heated with low calorific value gases is faced with the same situation. It was to be proved that purging every hour was not dangerous. Some steel plants use nitrogen or steam for purging, but the practice is expensive and unnecessary. If the spaces of gas flow are judiciously stream-lined, a pad of burnt gas remains between the stream of combustible gas and the air which follows. This pad is long enough to prevent mixing of combustible gas and air and thus excludes the risk of explosion. Four years experience in the pilot plant at Maizieres and a year long experience in the Dunkirk steel plant have shown that the method is quite safe.

Gas recovery devices

The second source of troubles is the connection of the converter mouth with the recovery device. A tight connection is obviously the first solution that one would think of; but even if absolute tightness is not required, the problem is difficult to solve. The shape of the converter mouth changes with time; wear of the bricks, distortion of the plates forming the mouth, deposits of steel and slag on the converter mouth as well as on the inlet of the recovery device exclude the possibility of a rigid metallic connection. Due to high temperatures a flexible connection is again impossible. Moreover, the connection will have to be shifted whenever the converter is charged. Such a device exposed to very hot and foul gases is liable to fail now and then.

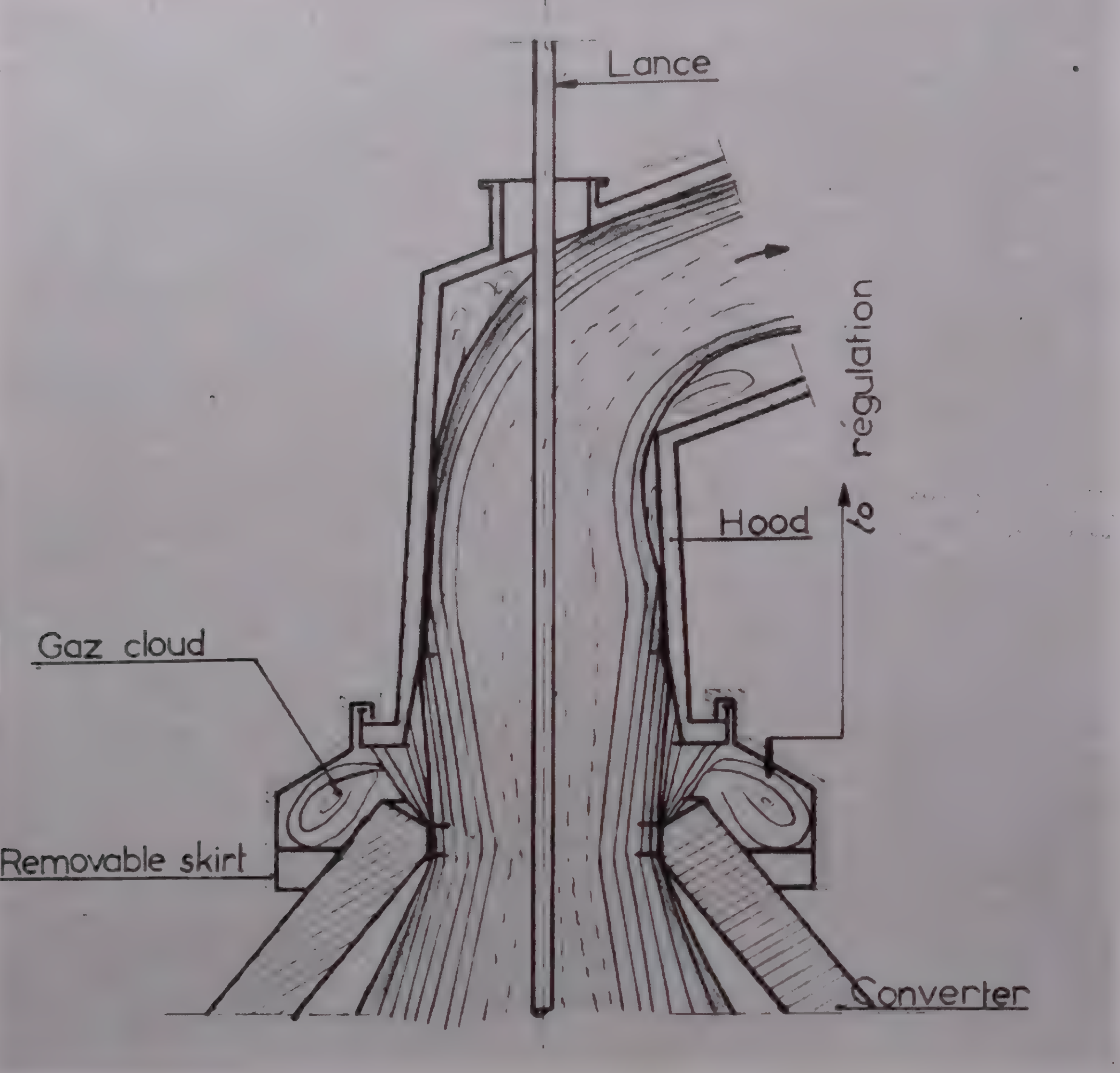
However, the Cie des Ateliers et Forges de la Loire (CAFL) has patented on April 21, 1959, a tight connection system which has been tested in the Dunkirk Steel Works. It has proved to be very efficient and has been adopted for industrial operations by YAWATA. Its only drawback is that the operator cannot watch the inside of the converter during the blow and should avoid any foaming of the slag and projections which might damage and even clog the connection. The blowing operation should therefore be carried out most carefully which entails a certain slowing down and a reduction in output.



2 *IRSID gas recovery apparatus*

To slove this difficulty, the Institute de Recherches de la Siderurgie Francaise (IRSID) developed and patented, on January 28, 1959, the 'open connection process' which consists in leaving a gap of several decimeters between the converter mouth and the inlet of the recovery device. The gas stream from the converter passes for a short while through ambiant air, burns there superficially, and enters the recovery system without carrying in too much of air if the draught is efficiently controlled, so that on the whole only 20% of the CO is burnt outside.

The recovery apparatus is shown schematically in Figs. 2 and 3. Its inlet is formed by a metallic skirt more or less open and definitely wider than the converter mouth. If the draught is properly controlled, an almost motionless cloud of hot gases occupies the upper part of the space below the skirt (Fig. 3). The gas stream passes through this cloud, drawn by the depression into the hood. When the draught is increased or decreased, the lower level of the cloud goes up or down



3 *Sectional view of the IRSID gas recovery apparatus*

allowing for a decrease or increase of the volume of unburnt gases stored for a while under the skirt. Slight accidental variations of gas output are thus ironed out. It will be seen later that the draught can be controlled by the height of the cloud which is another advantage of the system.

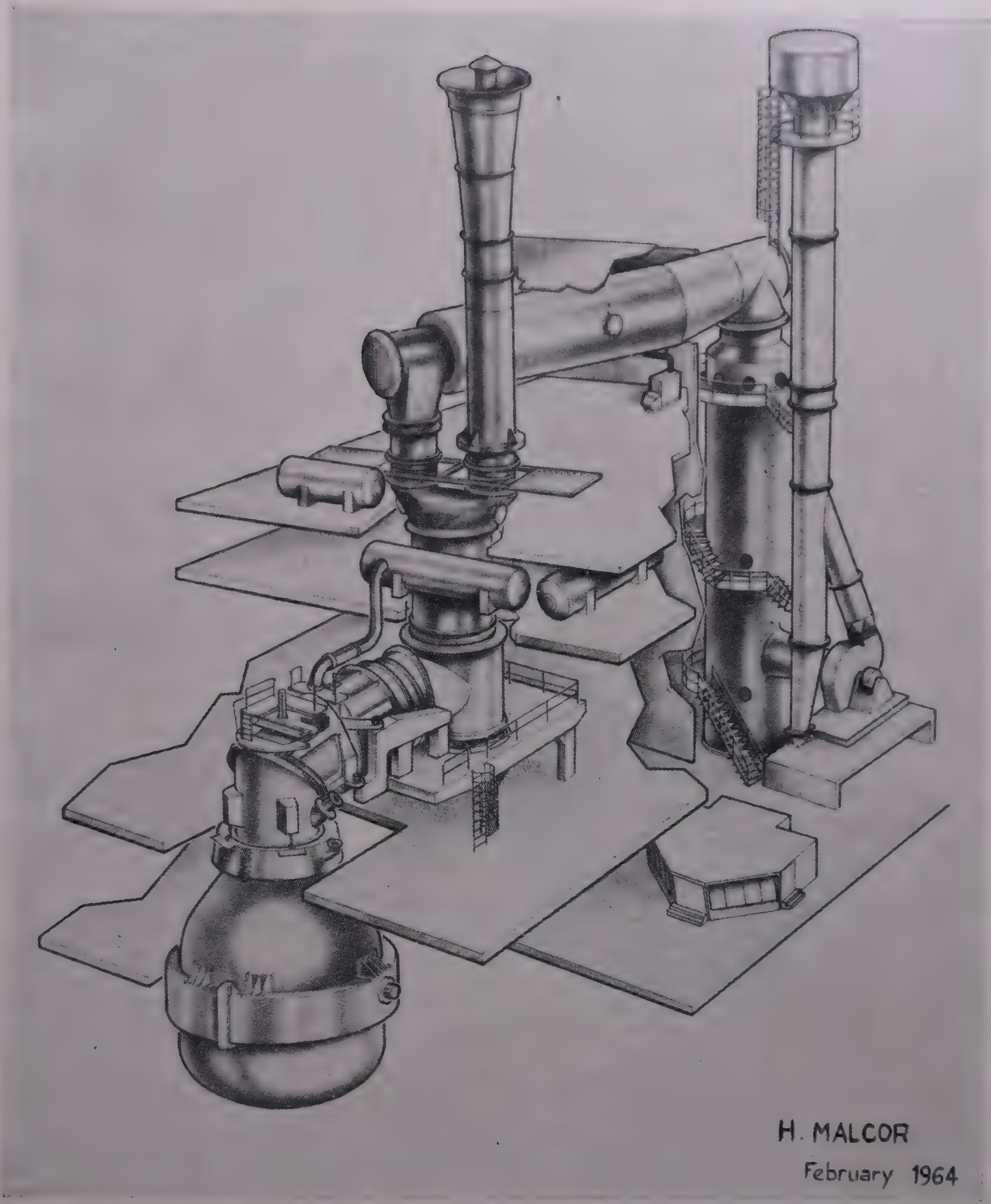
With the open connection system it is obviously possible to observe things at the mouth of the converter—projections, foaming—and thus prevent any damage to the inlet of the recovery system. It should be pointed out, of course, that the inlet is nevertheless nearer to the converter than that of a burnt gas cleaning installation and it is still necessary to keep projections and foaming to a minimum in order to protect the skirt and the hood. A certain constraint thus remains but it is less stringent than in the case of a tight connection and has the advantage of compelling the steel-maker to control the oxygen blast to avoid losses by projection. The open connection system was used by IRSID on their 6 ton OLP converter in the pilot plant of Maizieres les Metz as far back as November 1959. It is normally used in the LD steel plant of Usinor at Dunkirk since it was commissioned in February 1963. Until December 31, 1963 the Usinor plant produced 560 000 tons.

LD steel plant, Usinor

The steel plant consists of 3 LD converters of 125 tons each. Normal charge is 100 to 110 tons of pig iron and 20 to 30 tons of scraps. Blowing is done through a 200 mm lance with a hole of 67 mm diameter. The maximum oxygen output amounts to 360 Nm^3 per minute. The blow lasts for 24 minutes on an average and there is an interval of 55 minutes, from cast to cast.

With a new lining the converter mouth has a diameter of 2·20 m. The gas blown out of the converter enters into the hood built as a water jacket in the shape of a big inverted cone; its inlet diameter is 2·20 m. Consequently, skulls which sometimes stick to the inner surface of the hood can fall back into the converter which improves the yield. Under the hood is fixed a movable skirt, the lower part of which has a diameter of 5 meters. The water evaporated in the hood at the atmospheric pressure is evacuated to the atmosphere. The layout of the recovery and cleaning devices is shown in Fig. 4. The hood opens laterally upward into a boiler. As the recovery system had to be designed to suit the already existing plant the sharp bend imposed on the stream of gas could not be avoided.

Two of the boilers are tubular, the third is a simple water jacket. Substantial deposits of light dust were obtained in the tubular boilers, the bottom of which is nearly horizontal. Wide and readily accessible holes are provided in the water jacket boiler for easy evacuation. Gases leave the hood at temperatures of about 1 300°C. and the boiler at 1 200°C and then rise into a cooling tower with water jacket lining; at the upper part water is pulverized. The gases leave the tower at less than 400°C and penetrate into a hydraulic dust catcher of the Solivore type, built by the French Society VENTIL and consisting of a series of Venturis (Fig. 5). Dust content

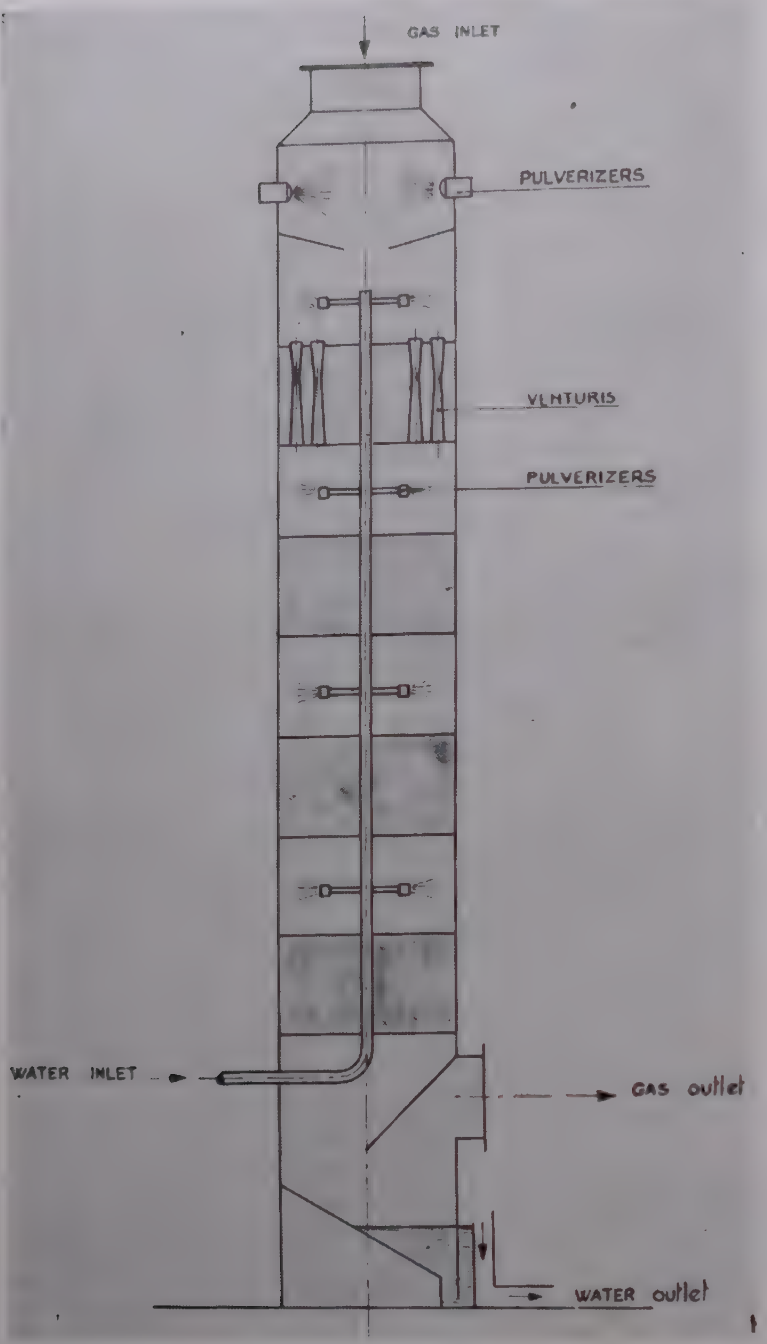


4 *General view of the gas recovery and cleaning installation at Dunkirk*

drops there from 130 gr to 150 mg per Nm^3, which amounts to a purification of 99·8%. Pressure loss is 150 mm of water and water consumption 0·1 m^3 per ton of pig iron. The purified gas passes through a 200 hp fan producing a draught of 380 mm. of water and is led to a torch, where, for the time being, it burns in the open. The recovery of the gas will be effected at a subsequent stage and no real difficulty is anticipated. The sludge easily settles down in a tank; the solids recovery amounts to about 8 kg per ton of pig iron. They hold more than 50% of metallic iron and can be sent to the sinter plant.

Draught control has a great importance; if the draught is too weak, the hood would blow carbon monoxide into the steel plant and if too strong, air would enter the hood and burn part of the carbon monoxide, thus reducing the calorific value of the recovered gas, and also increasing the temperature at the inlet of the exchanger and the heat to be evacuated there, which is even worse. It may be noted that gas temperature being already very high at this spot, any excess of air is neutralized by combustion and explosions need not be feared. This has been proved by the experience gained at both the Maizieres and Dunkirk plants.

During the first months of operation the draught was controlled by the pressure in the hood. The disadvantage of this method is that the holes of the hood, through which the pressure is measured, tend to get clogged by the projections. It was then decided to measure the pressure in the upper part of the skirt, as far as possible from the gas stream in a zone free from projections. Such holes are very seldom clogged; besides, no corrections are needed in this case for dynamic pressure because the gas cloud below the skirt is almost static



5 *VENTIL dust catcher.*

and the pressure at this point is closely linked to the height of the cloud. The pressure can be kept constant within ±0·1 mm of water.

Control of the draught by the pressure in the hood will be again tried in the Dunkirk steel plant after developing a device to prevent the clogging of hood holes. Such control is being smoothly effected for the past 4 years at the pilot plant of Maizieres les Metz where the controlling factor is not the pressure alone but a pressure factor + K (gas flow)^2. If automatic control fails, the operator can take over manually by judging the height of the fumes under the skirt and adjusting the draught accordingly. Provision of manual control is a definite advantage of the open connection process. The composition of the gas recovered varies from the beginning to the end of the blow. The average analysis is :

CO	CO_2	N_2	Calorific value
63%	17%	20%	2 000 cal/m^3

Per ton of pig iron, 75 Nm^3 of a gas containing 91% CO and 9% CO_2 are blown out of the converter. They are partially burnt by 23 Nm^3 of air giving 95 Nm^3 of gas ; 15 Nm^3 are lost at the beginning and the end of the blow and 80 are recovered.

Conclusion

The experience acquired in Maizieres les Metz and Dunkirk has thus shown that unburnt gases from oxygen blown converters can be safely recovered and cleaned with a good yield. The patented methods adopted help in decreasing the size and cost of the installation. Recovery of the latent heat of such gases will substantially increase the thermal efficiency of the steel process.

It must be recorded here that the bold decision taken by Usinor to try the gas recovery device in the Dunkirk steel plant was strongly supported by the High Authority of the Coal and Steel Community, who agreed to stand for a substantial part of the financial risks involved. Such encouragement is highly commendable indeed and of immense help towards adoption of new techniques and devices by the industries.

The New Stora Process for Ironmaking

A. N. Whiting

A. G. Raper

DURING the past two years, Stora Kopparbergs Bergslags A.B., Sweden, one of the iron and steel producing companies which lead the world in the development of iron and steel processes, have invented a new method of iron production and tested this on a pilot plant scale. This has given promising results and Stora are now installing a commercial scale plant at their Domnarvet Steelworks which will produce 50 000 tons per annum.

The process produces iron of controlled analysis from a wide range of differing types of iron ore, using carbonaceous material as reductant, and burning the carbon monoxide developed, to its fully oxidized state with oxygen.

This is achieved in a rotating vessel, similar in many respects to the Kaldo steelmaking furnace, the rotating facility assisting heat transfer and control over iron analysis and temperature.

The basic advantage offered by this process over the blast furnace and several other ironmaking processes, is that a low grade reductant is used which is fully oxidized before leaving the furnace and the carbon used as reductant forms carbon dioxide within the ironmaking furnace.

Background of direct reduction investigations

Over the last 10–15 years a number of direct reduction ironmaking processes have been proposed and developed to pilot plant and commercial scale throughout the world. It is important to realise that the circumstances surrounding the initiation of many of these developments have now radically altered.

Fifteen years ago, the bulk of the world's steel production was obtained using the open hearth or electric furnace processes. These processes could deal adequately with, as an alternative to scrap, cold iron in the form of briquettes, sponge or granules. The substitution of scrap by this cold iron in such furnaces gave only slightly increased conversion costs, and provided that the cold iron cost was lower than the prevailing scrap price, then the use of this product became economic.

The advent of the oxygen steelmaking processes has radically changed the background surrounding work on ironmaking processes, in that the low capital and energy requirements and hence low operating costs for steelmaking in oxygen converters can only be achieved by using a substantial molten iron charge although of course some cold iron can be absorbed. The introduction of oxygen steelmaking from a molten iron base, therefore, has reduced the demand for a cold iron product, and emphasised the need for liquid iron production.

Since increasing use will be made of oxygen steelmaking processes in the future, this paper deals only with those iron producing processes which result in a liquid product. Of these, the blast furnace and the electric smelting processes have received most attention, and developed further than any other liquid iron producing process.

The blast furnace

The blast furnace has a pre-eminent position in the ironmaking field and this is likely to continue for many years to come.

It is well known that the blast furnace can deal with almost any type of iron ore, either prepared or run-of-the-mine. The variation in type and extent of ore preparation results in a variation of the coke quantity consumed and the capital investment required for a given annual output.

The blast furnace suffers from the disadvantage that under all circumstances of operation, metallurgical coke is required and however well the burden is prepared prior to charging, the carbon in the coke can only be partially oxidized to carbon dioxide within the furnace.

It has been calculated that the limiting ratio of CO/CO_2 under optimum conditions is 1·861 : 1 by volume, or 65% carbon monoxide and 35% carbon dioxide. Using this ratio, the carbon will generate 4 500 K. cals against a theoretical 8250 K. cals available if 1 kg of carbon is oxidized completely to carbon dioxide.

The effect of this partial oxidation upon the thermal balance is well illustrated in Table I where results for the typical operation of two blast furnaces working on a part sinter burden are given.

TABLE I **Operating data for blast furnaces charged with a part sinter burden**

Item	Blast Furnace A	Blast Furnace B
Iron make	1 400 tons/day	1 430 tons/day
B.F. Coke rate/ton iron	763 kg	694 kg
Sinter Coke rate/ton sinter	59 kg	82 kg
Burden wt./ton iron	1 945 kg	2 000 kg
Sinter % Burden	44·9%	59·0%
Unscreened ore % Burden	31·9%	—
Screened ore % Burden	23·2%	41·0%
Slag/ton iron	403 kg	514 kg
CO/CO_2 volume ratio	1·91	1·90
Steam for blowers	34 400 kg/hr	34 100 kg/hr
Total gas make/ton iron	3 260 n.m.^{3}	3 080 n.m.^{3}
Gas for stove heating/ton iron	910 n.m.^{3}	905 n.m.^{3}
Surplus gas/ton iron	23,40 n.m.^{3}	21,70 n.m.^{3}
Gas calorific value (gross)	854 K. cals/m^3	807 K. cals/m^3
Surplus energy available therms/ton iron	1 995 M. cals	1 750 M. cals

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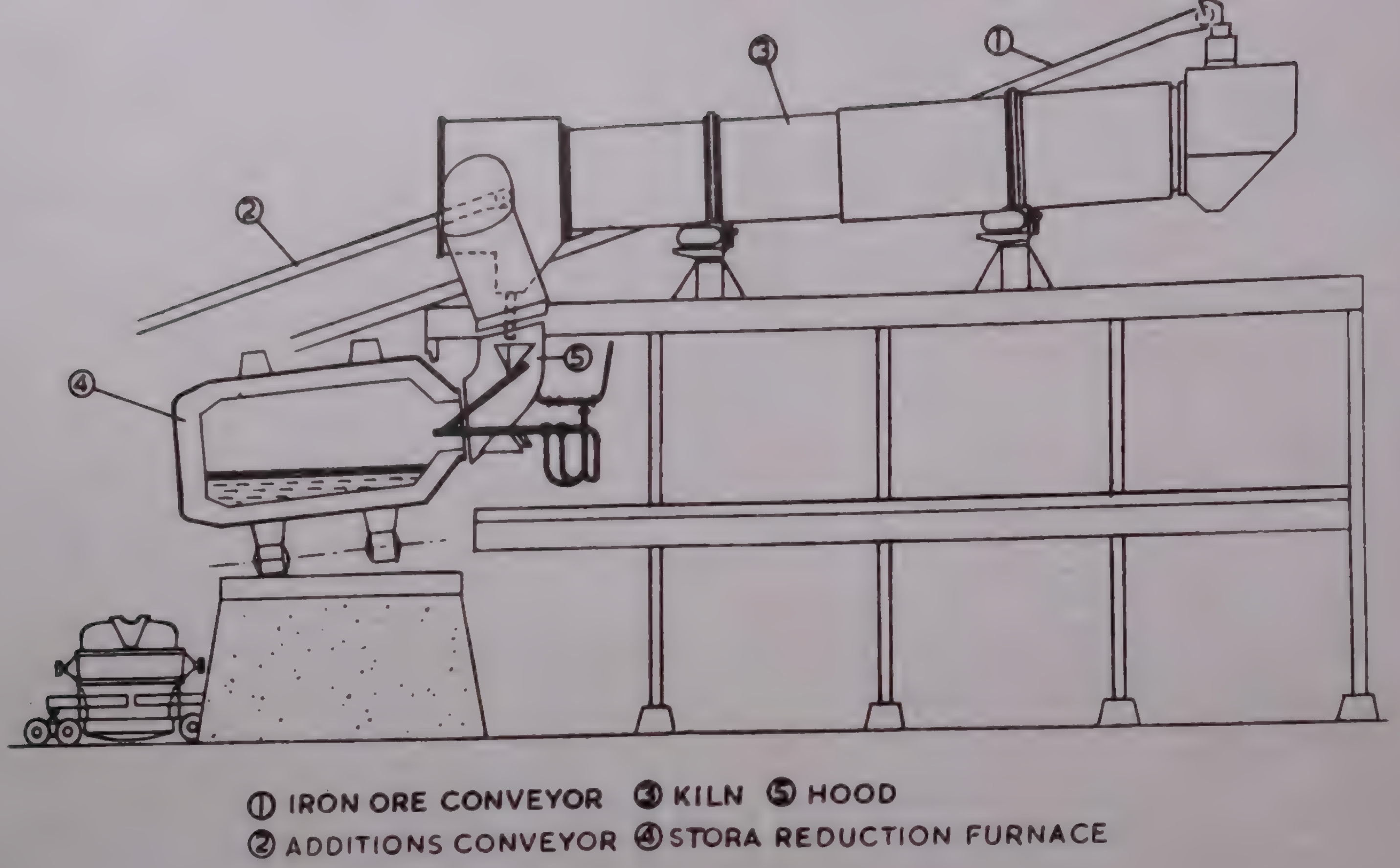
Mr A. N. Whiting, General Manager, and Dr A. G. Raper, Metallurgical and Technical Manager of Steel Processes Division, Davy and United Engineering Company Limited, Sheffield, England.


①
②
③
④
⑤
① IRON ORE CONVEYOR ③ KILN ⑤ HOOD
② ADDITIONS CONVEYOR ④ STORA REDUCTION FURNACE

1 *Stora ironmaking process equipment*

It is seen that a typical blast furnace may generate a surplus of energy of the order of 1750-2000 M. cals per ton of iron made. If the blast furnace is associated with coking it has been shown (ref. 1) that the surplus is increased and a typical example is shown in Table II.

TABLE II Thermal balance for coke ovens and blast furnaces charged with a part sinter burden

Coal requirement	1·06 tons/ton hot metal
Energy input per ton hot metal in M. cals (Excluding electric power)	
Coking coal charged into ovens	7 220
Steam for by-products	540
Total	7 760 M. cals
Energy output per ton hot metal in therms	
Heat in hot metal (sensible and chemical)	688
Blast furnace gas surplus after underfiring ovens and heating stoves	935
Coke oven gas	1 320
Coal tar fuel	210
Crude benzol	70
	3 223 M. cals

From Table II it is seen that a typical heat surplus due to the non or partial oxidation of hydrocarbons during the coking and smelting process is 2 535 M. cals per ton of pig iron.

An integrated works will of course use a large proportion if not all of the gas generated in this way for steelmaking, reheating, lime burning and power generation, etc.; if open-hearth steelmaking is practised the entire production will probably be required. If oxygen steelmaking is used this is not certain to be the case and an excess of gas may result. The overproduction will be more serious at intervals when for example the mill is off line for maintenance.

Even if the problem of surplus gas does not arise it should be remembered that the low grade fuel produced is derived from expensive high grade metallurgical coal or coke which may not be the most economical way of satisfying the energy requirements of the integrated works.

Thus whilst the blast furnace remains and will remain for many years the major iron producing unit, the problems of gas production and the demand for metallurgical coke may restrict the economic adoption of the process under certain situations.

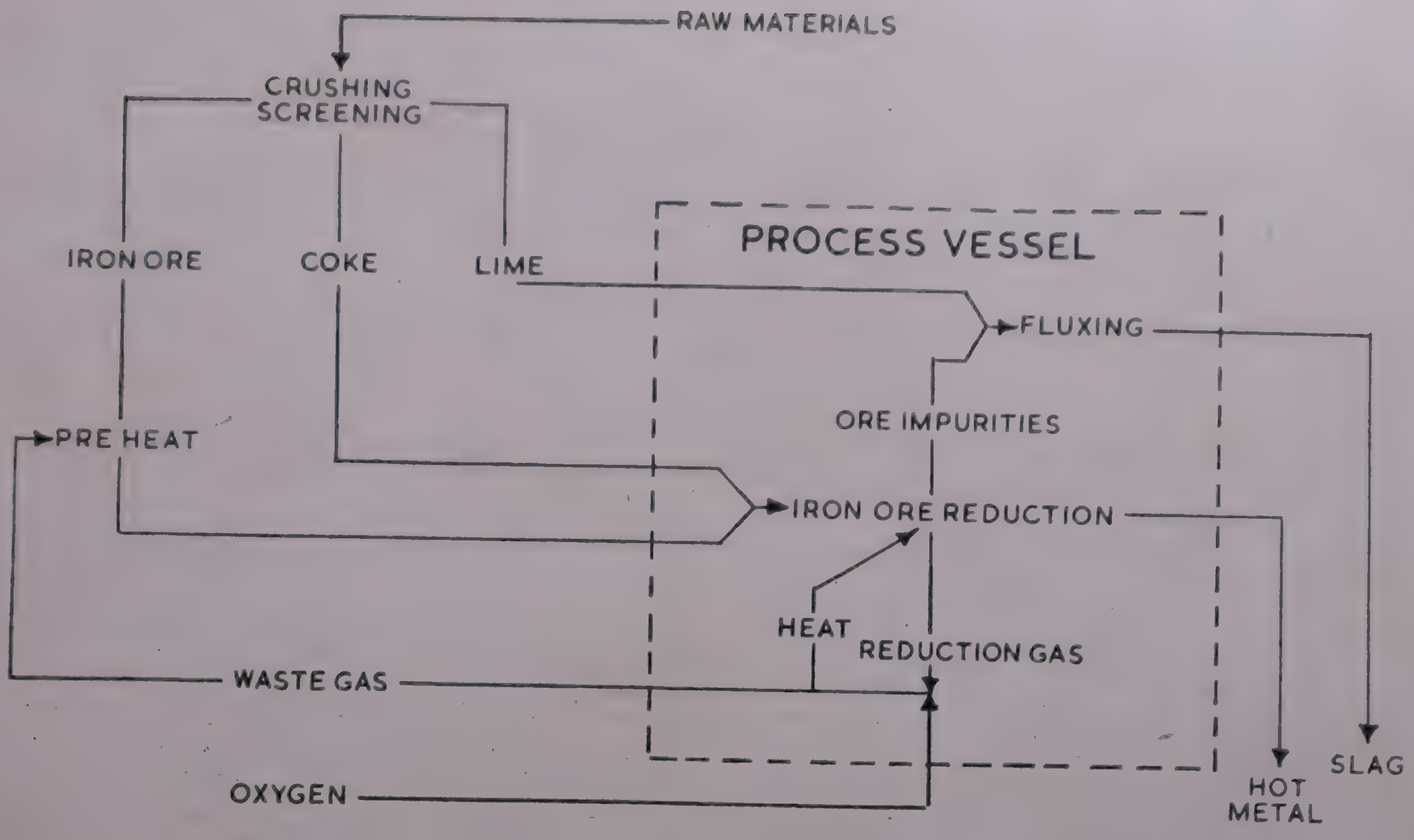
Electric smelting

A number of electric smelting processes have been developed which possess the important advantage of producing a liquid iron product. Furthermore high grade metallurgical coke is not required. Until fairly recently the processes were operated without pre-reduction of the ore which lead to power requirements of 2 000 kW hr/ton and coke requirements of 350–400 kg/ton of hot metal (ref. 2). The process has, however, recently become more attractive in conditions where power costs are somewhat higher by the use of pre-reduction either in vertical shafts or rotary kilns.

Typical operating data of a furnace fed from a rotary pre-reduction kiln are given in Table III. Ore is fed direct to the counter current fired kiln without pretreatment other than crushing and screening (pelletising may be required under some conditions) together with raw coal. The kiln is fired with pulverised fuel and the mix of the ore with its associated oxygen pre-reduced to 50% of the original value with the carbonised coal is transferred hot to the electric smelter.

From Table III it is seen that whilst the processes use a smaller quantity of coal when compared with the blast furnace which in addition need not be of metallurgical coking quality, again only partial oxidation is achieved and the heat in the top gas is again high.

Again as in the case of the blast furnace, opportunity exists on an integrated works for using the gas in other areas. For example up to 50% of the gas make may be uned on the pre-reduction kiln for control heating and is



2 *Stora ironmaking process flowsheet*

TABLE III

Iron ore/ton iron	1·80 tons
Lump coal/ton iron	810 kg
Limestone and dolomite/ton iron	410 kg
Pulverised fuel (kiln firing)/ton iron	150 kg
Power consumption/ton iron	1 400 KWhr.
Slag production/ton iron	750 kg
Gas volume/ton hot metal	305 n.m^3
CO/CO_2 ratio by volume	3·75
Calorific value (gross)	2 270 K.cals/m^3
Energy contained in outlet gas/ton hot metal	692 M.cals

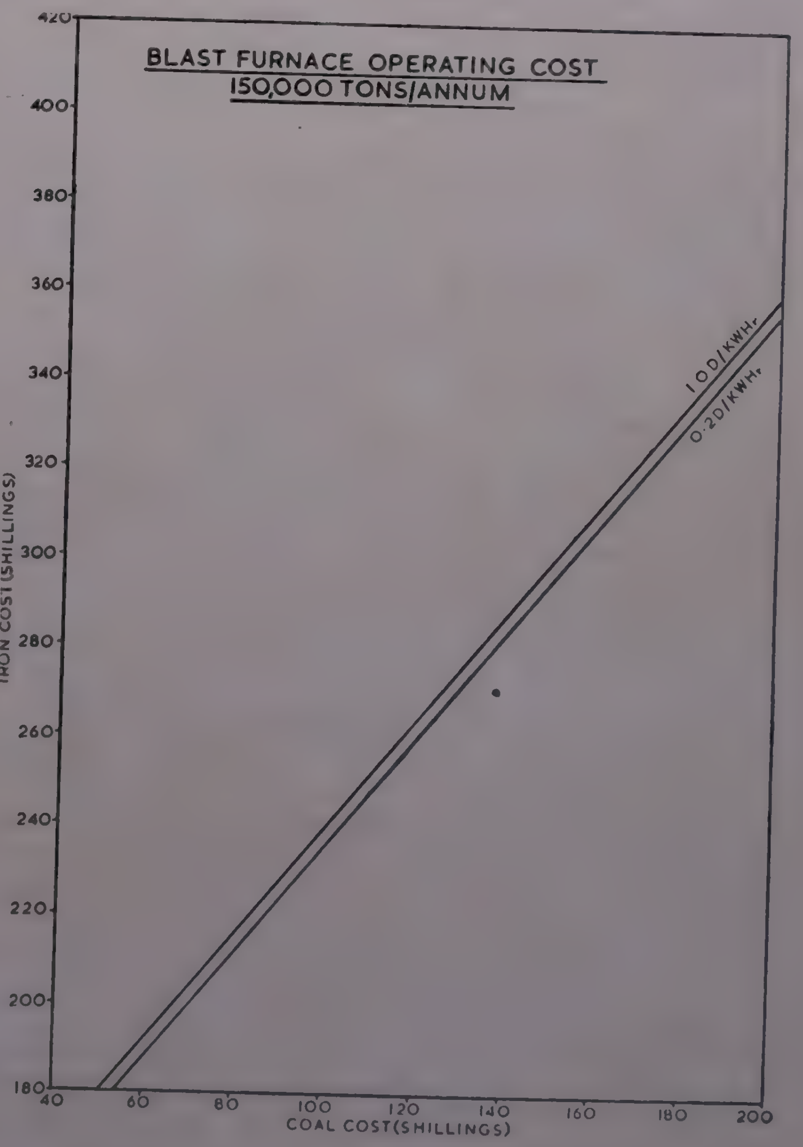
part substitution of the pulverised fuel. It is therefore unlikely that even for limited periods a gas surplus would be a problem on integrated works.

However in addition to the gas loss from the smelter there is a further heat loss in some of the coal volatiles and the sensible heat of the burnt products of combustion emitted from the kiln which may amount to 1 500 M.cals per ton of iron. This loss may be somewhat reduced in a co-furrent fired kiln but it may be sufficient particularly if associated in a number of situations.

The Stora Ironmaking Process

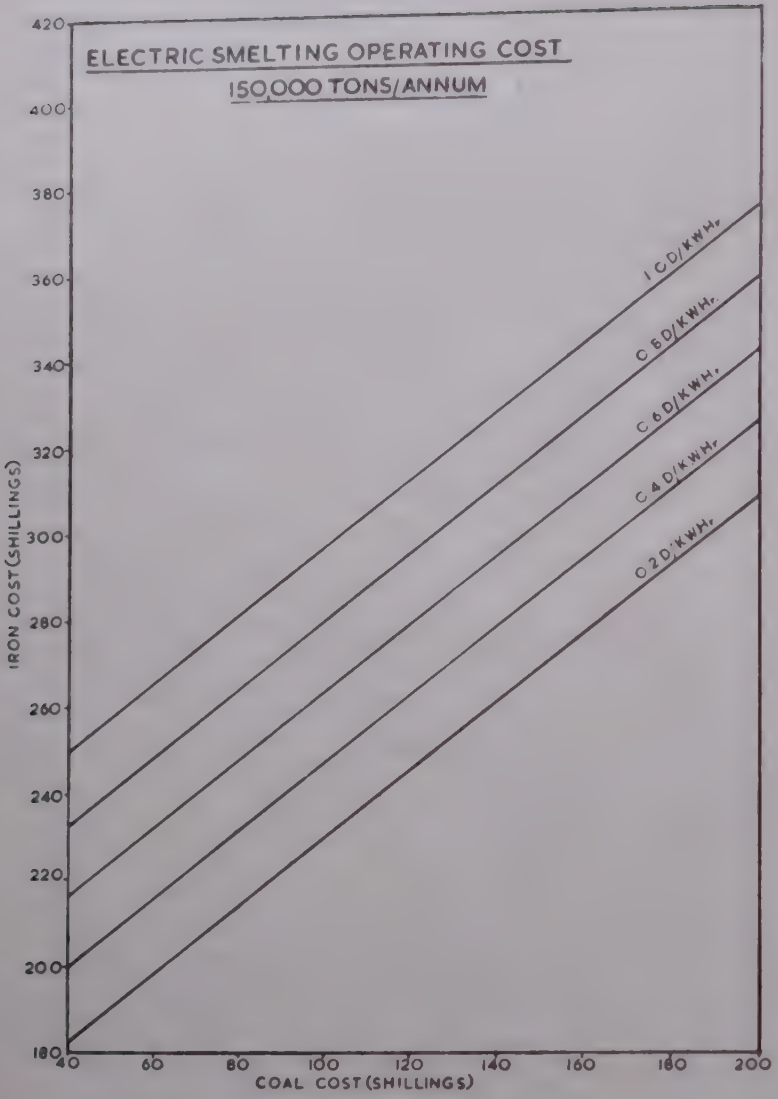
The new Stora Ironmaking Process possesses a number of features which are highly desirable. Some of the features suggest that it will become highly competitive with other forms of ironmaking in a number of situations.

A liquid product is produced using relatively small quantities of low grade carbon reductant such as coke breeze and certain types of coal. No metallurgical coking coal is required and little ore pretreatment other than crushing is necessary.

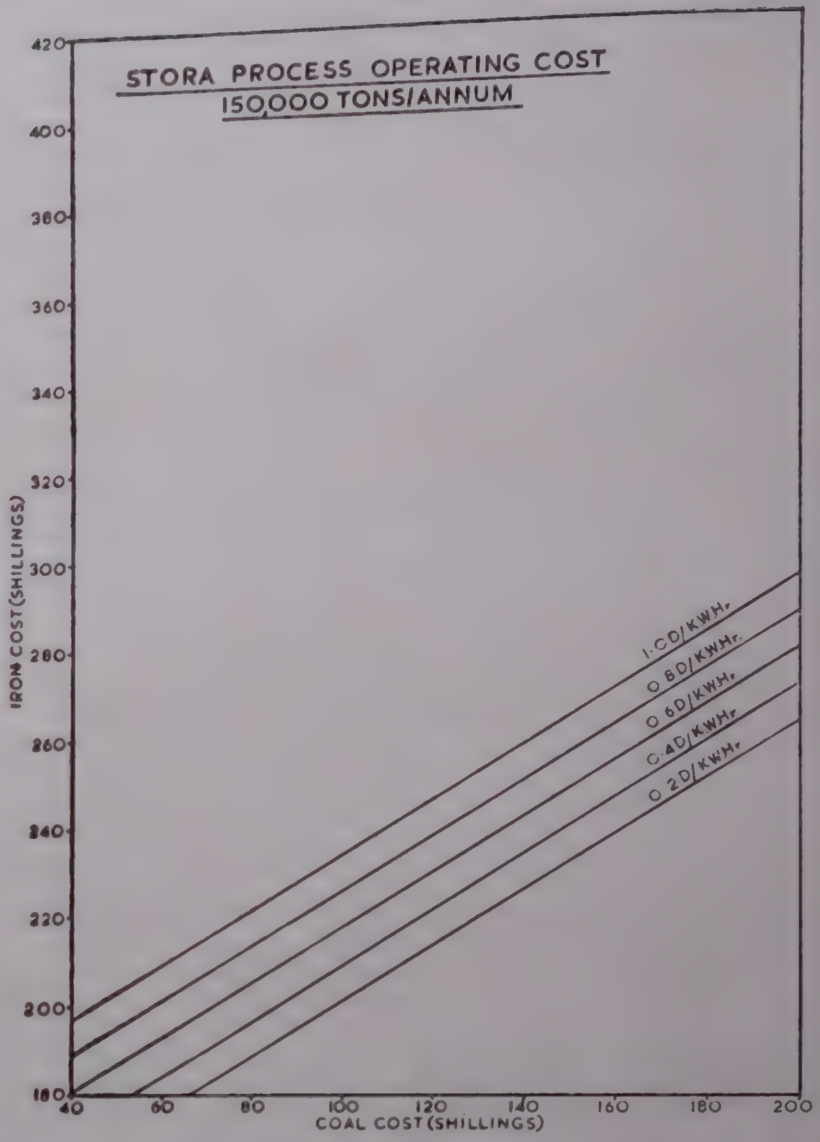


3 *Blast furnace operating cost 150 000 tons/annum*

A further major advantage of the process is related to the low carbon requirement. It has been shown that a characteristic of other ironmaking processes is the partial oxidation of the carbon reductant. In the Stora process full oxidation to carbon dioxide is achieved. The heat released is largely recovered either within the smelting unit proper or in an ore preheating kiln. In this way there is no chemical heat loss in the outgoing gases and the sensible heat loss is limited to approximately 375 M.cals per ton of iron at the exit of the preheat kiln.



4 *Electric smelting operating cost 150 000 tons/annum*



5 *Stora process operating cost 150 000 tons/annum*

The process utilizes a rotating furnace into which carbon, ore and oxygen of 95% purity are fed. The rotating furnace is of similar design to the Kaldo steelmaking furnace and rotates at approximately 30 r.p.m. whilst the reactants are fed continuously into the furnace through specially designed lances and feeding equipment.

The reduction of ore is achieved by intimate contact with carbon, and the resulting carbon monoxide gas is burnt to carbon dioxide within the free space above the liquid and solid layers. The combustion of the carbon monoxide with oxygen releases heat which is transferred to the bath for the endothermic iron oxide carbon reaction. The rate of heat transfer is greatly improved by the rotation of the furnace.

Under these conditions, the off-take gas emitted from the furnace mouth is at a substantially higher temperature than the off-take gas, for example, from a blast furnace; however the volume of gas evolved from the furnace mouth per ton of iron produced, is much smaller than that produced per ton of iron by the blast furnace by virtue of the fact that no nitrogen is introduced into the system.

The high temperature waste gases are directed into a pre-heating kiln and utilized in raising the temperature of the ore charged to the smelting furnace to approximately 700°C. In so doing, 40% of the sensible heat in the off-take gas is utilized before the waste gas is discharged to atmosphere, via a stack after suitable cleaning.

Fig. 1 shows in diagrammatic form, the equipment required for the process, and Fig. 2 is a materials flow sheet.

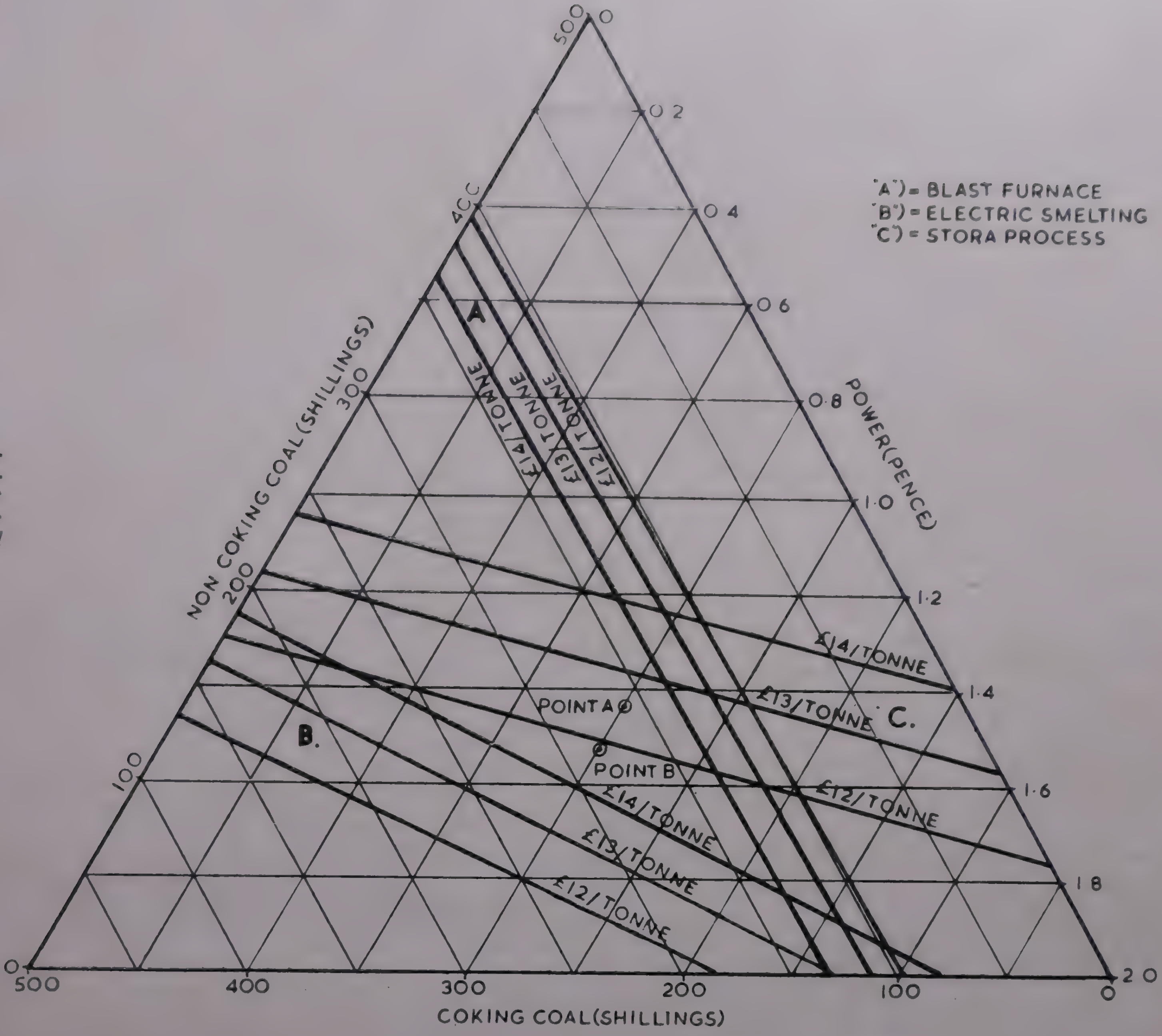
Work so far performed on both small 5 ton furnace and a 30 ton furnace tests has indicated that the carbon consumption per ton of iron produced is no more than 450 kg (corresponding to 510 kg of coke with 88%C).

Approximately 385 kg of oxygen are required per ton of iron produced, i.e. about 300–350 n.m.^{3}. Investigations may show it is possible to substitute some part of the oxygen with pre-heated air, although the extent may be restricted by the need to burn all the carbon dioxide within the furnace.

However, at a cost of ld. per normal m^3 of oxygen, a cost which should be achieved in view of the quantity required, the oxygen cost will be Rs 29 per ton of iron produced. This expenditure can be compared with the saving resulting from relatively low energy cost for reduction, i.e. a saving of at least 250 kg and possibly 500 kg/ton iron of high grade coke required for blast furnace practice, or alternatively the equivalent of 1 000–1 200 kWhr/ton iron in the case of electric smelter.

Capital and operating cost studies

To evalute the type of situation under which the Stora process would become economically attractive it is necessary to calculate capital and operating costs for the blast furnace, electric smelting and the Stora processes respectively.



6 *Comparative ironmaking production costs of blast furnace, electric smelting and Stora process*

However, it can often be misleading to give general cost comparisons of this nature. Capital costs depend greatly upon the nature of the raw materials available, plant location and customer requirements. For example in the case of a blast furnace and coking plant the extent of by-product recovery plant installed will be related to markets and availability of capital. Alternatively the ore type will dictate whether or not pelletizing equipment is necessary for electric smelting. Similar difficulties arise with operating cost comparisons.

Capital costs

In spite of the problems outlined it was considered that the cost aspects of the processes concerned were so important that some indication should be given. Table IV gives a range of capital costs for the processes under consideration. A production level of 150 000 tons per annum has been assumed derived from unprepared ore containing 60%Fe and washed screened coal, coking or non-cocking as the case may be. The estimated prices stated are complete and include civil engineering and erection costs.

The blast furnace with coke ovens work an unprepared burden and the minimum of by-product recovery plant is installed. The electric smelting plant includes ore crushing, pelletizing and a rotary pre-reduction kiln. Power plant costs are not included. The Stora process plant is assumed to comprise of two furnace units each with its associated ore preheating kiln. The oxygen plant costs are included but lime burning and power plant costs excluded.

TABLE IV Approximate capital costs for ironmaking plant
(Annual output 150 000 tons)

Process	Approximate range of capital cost @ sterling/annual ton
Blast furnace and coke ovens	17–25
Electric smelting	20–24
STORA process	16–20

Although as stated previously no firm conclusion is possible from Table IV due to variable conditions it does however indicate that at least for the range of output and conditions assumed the equipment cost for the Stora process is no greater than for equivalent ironmaking processes.

Operating costs

Typical operating costs have been calculated for similar conditions as were considered in the capital cost section. Assumed operating data and the operating cost sheets are given in the Appendix.

It can be seen from the cost sheets that the iron produced in a particular locality assuming a fixed ore cost and process iron yield from any of the three processes studied will be composed of an energy cost and a further cost which can be called a fixed cost. The fixed cost comprising flux, labour, lining and maintenance costs, etc. will in general remain fairly constant from locality to locatity for each process but may be adjusted if required. The energy cost i.e. coking or non-coking coal and power costs may vary considerably with locality and will therefore affect process choice.

These assumptions although approximate only allow Figs. 3, 4 and 5 to be drawn which indicate the effect of energy cost upon iron cost produced from the three processes. Figures 3, 4 and 5 can then be used to compile Fig. 6 which is a composite cost graph and shows the effect of energy cost upon the iron production cost for any of the three processes. This can be used under any particular situation to determine which process is likely to be most attractive from an operating cost standpoint. The use of the graph is demonstrated in the example below. If any of the costs shown in the Appendix differ from those shown then Fig. 6 may be redrawn after recalculating the costs with corrected data.

Example

e.g. Assumed cost of coal	£8/tonne
Assumed cost of non-coking coal	£6/tonne
Assumed cost of power	0·8d./kWhr.

Using the above assumed local costs, points A and B are plotted. It can be seen from these points that the cost of iron, by the three processes will be as follows :

(*a*) Blast furnace	£15.5.0/tonne
(*b*) Electric smelting process	£15.0.0/tonne
(*c*) Stora process	£12.0.0/tonne

Conclusions

Although the development of the Stora ironmaking process is still at an early stage it is already clear that the process has a potentially large field of application.

The equipment composed principally of a rotary furnace is relatively simple and a liquid iron of controlled composition and temperature is produced. This provides an ideal feed stock for oxygen steelmaking processes or foundry applications.

Low phosphorus pig iron can be produced from high phosphorus ore when basic linings are used. Crushing only is required as preparation for the ore and fuel and low grade fuels such as coke breeze and certain types of coal can be used as fuel.

Capital and operating cost comparisons have been undertaken and although these can be considered as approximate only and liable to modification under any particular situation, they indicate that at a liquid pig iron requirement of 150 000 tons per annum. the process is extremely competitive with other processes where metallurgical coke and power costs are relatively high.

Acknowledgements

The authors wish to express their thanks to the Directors of Stora Kopparbergs Bergslags A.B., Sweden and also of the Davy and United Engineering Company, England for granting permission to publish this paper. Special thanks are due to Mr A. Josefsson, Head of the Research Department, Stora Kopparbergs Bergslags A.B.

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Appendix

Operating costs have been derived for ironmaking by the processes described previously : (*a*) the blast furnace (*b*) the electric smelting process and the (*c*) Stora ironmaking process.

The same material costs have been used throughout. Many of the material costs and other costs such as labour and maintenance generally will not vary greatly from location to location and these have been summed and extracted from the cost tables 5 to 8, and called the fixed cost. This fixed cost may be adjusted according to location if required. The remaining cost or energy cost comprising coking or non-coking coal and power may vary considerably from location to location thereby affecting choice of process and for this reason a range of costs has been taken for these items.

Coking coal	... £0–£10/ton (in £2 increments)
Non-coking coal	... £0–£10/ton (in £2 increments)
Power	... 0d.–1d./ton (in 0·2d increments)

In the three processes it is assumed that an Fe yield of 100% is attained from the 60% Fe ore. It is recognised that this cannot be attained in practice but a similar yield is anticipated for all processes and, therefore, the assumption is adequate for comparison purposes. For this reason the cost of iron ore per ton of iron is taken to be common to all processes.

It will be seen that the ironmaking cost C_I can be expressed, therefore, as follows :

$$C_I = K + k_1 + k_2$$

where K = Fixed production cost

k_1 = Variable coal cost.

k_2 = Variable power cost.

Using the equation above, for the three ironmaking schemes from Tables VI, VII and VIII, Figs. 3, 4 and 5 have been drawn up respectively. These illustrate the cost of iron against cost of coking and non-coking coals with varying power costs.

From Figs. 3, 4 and 5 Fig. 6 has been drawn up.

TABLE V Conversion cost coal—coke
(Blast Furnace)

Item	Requirement per ton (kgm)	Material cost/ton (shillings)	Cost per ton coke (shillings)
Coal	1 335 kg	40–200	53·40–267·00
Power	20 kW hr	0·6d.	1·00
Refractories	—	—	3·50
Steam	500 kg	10	5·00
Miscellaneous	—	—	2·00
Maintenance and Consumables	—	—	5·00
Spares	—	—	5·00
Labour	—	—	5·00
General Administration	—	—	5·00
Total			84·90–298·50
Small coke credit	140 kg	40	5·60
Coke oven gas credit			10·00
Tar credit	70 kg	60	4·20
Total			19·80
Cost per ton coke			65·10–278·70

TABLE VI (*a*) **Blast Furnace**—Basis 150 000 tons iron/annum

Item	Requirement per ton (kgm)	Material cost/ton (shillings)	Cost per ton iron (shillings)
Iron ore	1 670 kgm	35	58·45
Limestone	300 kgm	30	9·00
Coke	900 kgm	65·10–278·70	58·59–250·83
Power	50 kWhr	0·2d–1·0d	0·83– 4·17
Refractories	—	—	5·00
Miscellaneous	—	—	2·00
Maintenance and consumables	—	—	10·00
Spares	—	—	6·00
Labour	—	—	7·00
General administration	—	—	15·00
Total			1 1·87–367·45
Gas credit			7·00
Cost per ton iron			164·87–360·45

TABLE VII (*b*) **Electric smelting**—basis 150 000 tons iron/annum

Item	Requirement per ton (kgm)	Material cost/ton (shillings)	Cost per ton iron (shillings)
Iron ore	1 670 kgm	35	58·45
Limestone	300 kgm	30	9·00
Coal	775 kgm	40–200	31·00–155·00
Coke	20 kgm	171·90	3·44
Electrode paste	10 kgm	500	5·00
Power	1 000 kWhr	0·2d–1·0d	16·67– 83·00
Refractories	—	—	5·00
Fuel oil	35 kgm	170	5·95
Miscellaneous	—	—	4·00
Maintenance and consumables	—	—	12·00
Spares	—	—	9·00
Labour	—	—	10·00
General administration	—	—	15·00
Total			184·51–375·17
Top gas credit			1·00
Cost per ton iron			183·51–374·17

TABLE VIII (*c*) **Stora Process**—basis 150 000 tons iron/annum

Item	Requirement per ton (kgm)	Material cost/ton (shillings)	Cost per ton iron (shillings)
Iron ore	1 670 kgm	35	58·45
Coal	614 kgm	40–200	24·56–122·80
Power	476 kWhr	0·2d–1·0d	7·93– 39·67
Lime	150 kgm	90	13·50
Compressed air	—	—	1·70
Refractories	—	—	5·00
Miscellaneous	—	—	4·00
Maintenance and consumables	—	—	10·00
Spares	—	—	10·00
Labour	—	—	10·00
Oxygen (labour and water)	—	—	5·00
General administration	—	—	15·00
Total			165·14–295·12
Cost per ton iron			165·14–295·12

Short Rotary Furnace and its Application in the Treatment of Battery Scrap

W. Schwartz
W. Haase

WITH rapidly increasing automation and mechanization during the past decades, recovery of lead from scrap metals has gained great importance in highly industrialized countries, particularly as a large proportion of lead production is consumed in the manufacture of batteries.

In the year 1962, the United States consumed 980 486 metric tons of lead while in the same period, 380 900 metric tons of the metal were recovered from scrap materials (secondary lead) which represents 39% of the consumption. In the same year, the lead requirement of the USA for the manufacture of batteries was 187 945 tons as hard lead and 174 063 tons as lead oxide, i.e. a total of 367 008 tons which corresponds to 37% of the total lead consumption and is more than 93% of the secondary lead production. In Germany 22% of the total lead production is used for batteries. Considering that a lead battery lasts for 2 to 4 years, these figures clearly show the significance of battery scrap treatment in the lead industry of technically developed countries.

Lead batteries contain an average of 70–80% of lead and the overall chemical reaction taking place may be characterized as follows :

$$2\text{Pb SO}_4+2\text{H}_2\text{O} \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftarrows}} \text{Pb}+\text{PbO}_2+\text{H}_2\text{SO}_4.$$

Battery scrap

A new lead battery consists essentially of anode plates (porous lead dioxide in a lead grid) and cathode plates (sponge lead) separated from each other by perforated plastic sheets. The cathode plates are made of a lead alloy containing 5–8% antimony and they should contain the least possible amounts of copper, iron, and bismuth ; a bismuth content as low as 0·01% has proved harmful. Old batteries are generally in a discharged state and their cathodes consist of porous lead plates coated with lead sulphate and their anodes of porous lead dioxide plates coated with lead sulphate.

In addition to the manual separation of battery scrap into plastic, brass and copper materials, there have been frequent attempts to separate completely the lead dioxide from the antimonial metal in order to smelt them separately. However, this process is only practicable if the oxide can be kept completely free from antimony and if smelting can be carried out to obtain soft lead. Depending on local conditions, battery scrap is treated in shaft furnaces, reverberatory furnaces and, less frequently, in electric furnaces.

Treatment of battery scrap

Treatment in the shaft furnace is only economical if the furnace can be fed with the same material for a considerable time ; this calls for large quantities of battery scrap which are not readily available. It is not advisable to treat the battery scrap together with lead sinter as most of the antimony goes into the bullion which has to be refined again.

In both cases, the high blast pressure required for large-size shaft furnaces results in heavy dust losses because the oxide no longer adheres firmly to the grid plates. It is impossible to avoid these dust losses, even by using high return slag rates.

Treatment of battery scrap in electric furnaces is hardly economical on account of the high power costs involved.

The reverberatory furnace, presents its own characteristic disadvantages such as low thermal efficiency, heavy attack on the brick lining at the skim line, etc. Moreover, the resulting slag is in most cases rich in lead and has to be further treated in a shaft furnace.

The short rotary furnace is very well suited for the treatment of battery scrap. It offers the possibility of separating the scrap at a high rate into antimonial lead and a low-lead slag, without the disadvantages of the reverberatory furnace. The short rotary furnace has also given excellent results in the treatment of lead-bearing intermediary products and lead ashes as well as in the self-fluxing reaction smelting of sintered lead concentrates[1, 2].

The short rotary furnace

This is a furnace for smelting in reducing and oxidizing atmospheres. The smelting chamber is a steel drum with refractory lining rotating around a horizontal axis. The diameter of the furnace is approximately equal to its length (Fig. 1).

Pulverized coal, gas or oil are used as fuels. The temperatures reached in this furnace vary between 1 000

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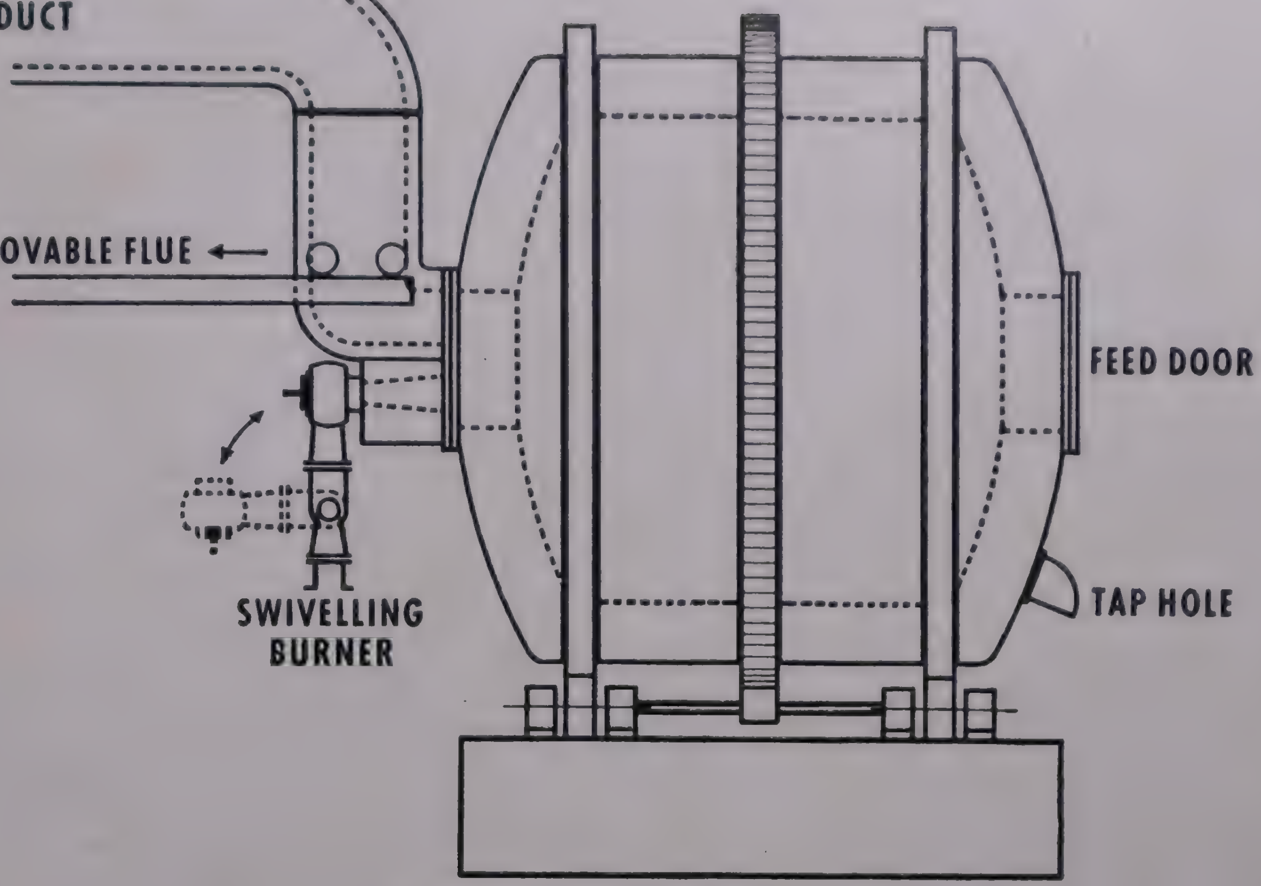
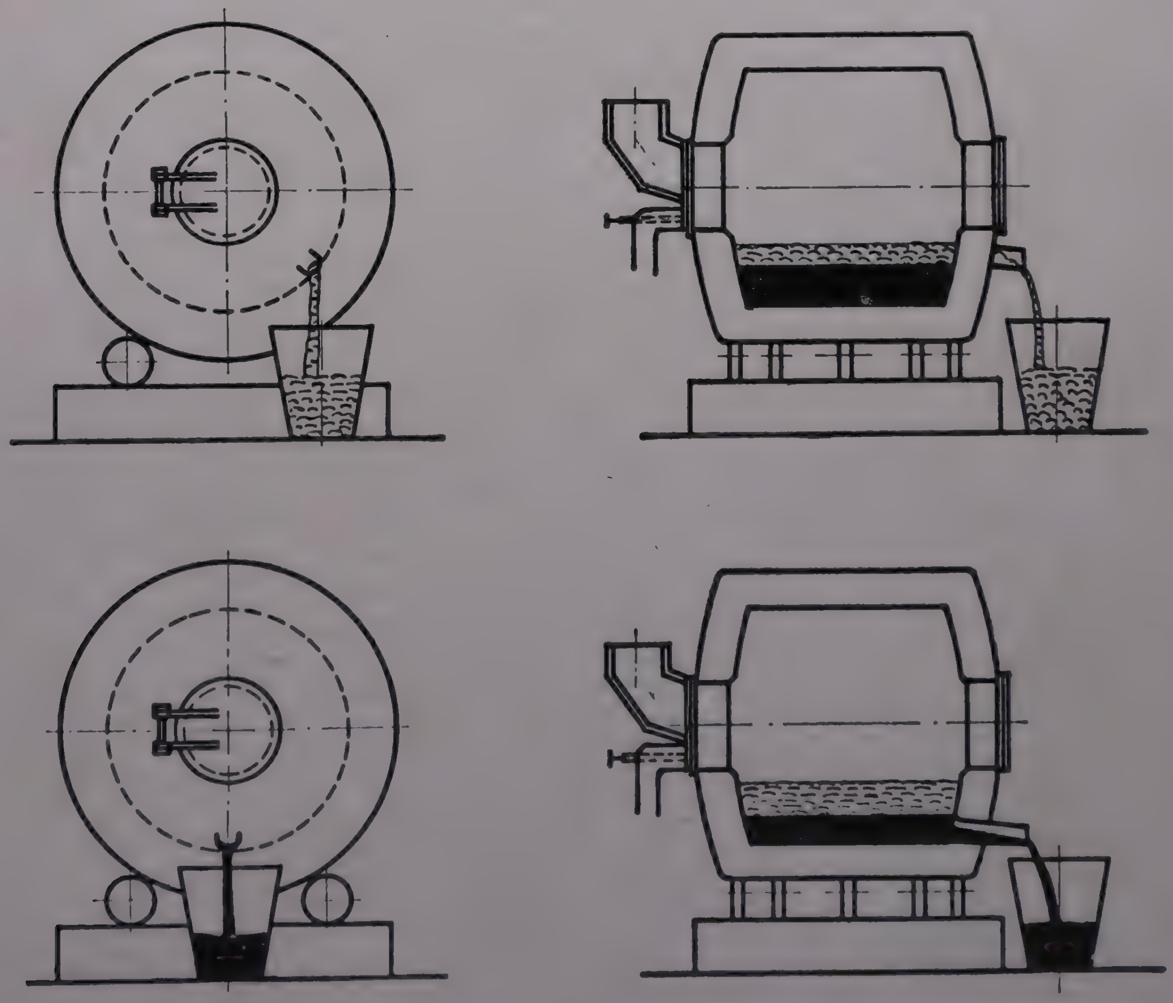

EXIT GAS DUCT
MOVABLE FLUE
FEED DOOR
SWIVELLING BURNER
TAP HOLE

1 *Short rotary furnace*


TAPPING OF SLAG
TAPPING OF METAL

2 *Tapping of slag and metal from the short rotary furnace*

and 1 500°C. The burner is easily accessible and can be swung away. The burner flame enters through a central opening in the rear wall of the furnace and the exit gases leave the smelting chamber through the same opening so that charging, tapping, etc. can be carried out from the opposite front wall.

The furnace is charged through a feed door in the front wall; for the treatment of battery scrap, a feeding chute is usually placed before the open furnace door. Charging boxes of 1 to 2 tons capacity are emptied by a crane into the funnel of the feeding chute from where the material slides into the furnace. This procedure may be repeated several times for each batch.

In order to cut down fuel consumption and avoid undesirable deposits in the dust filter, it has proved advisable to remove, as far as possible, all glass and plastic materials from the battery scrap. The plastic materials are usually burnt in a simple chimney. Any resulting lead ashes are also treated in the short rotary furnace together with the lead sulphate sludge (after pelletizing, if desired).

The short rotary furnace can be moved to bring the tap hole to the desired level. This permits the tapping of lead when the hole is at a low level, and that of metal-free slag from the bath surface when the tap hole is at a higher level (Fig. 2).

To tap the metal, a ladle is placed in front of the furnace which is rotated until the tap hole is in the lowest position and the metal is released by pulling out an iron rod from the tap hole. The metal flow may be stopped at any moment by rotating the furnace so that the tap hole rises above the metal level. The slag can be skimmed without removing any metal by opening the tap hole when it has reached its highest position and by rotating the furnace slowly until the slag has been decanted. The intermediate layer between slag and metal, which has a high metal content, is usually left in the furnace. For opening or closing the tap hole, the furnace is rotated to raise tap hole above the metal and slag.

The spherical shape of the short rotary furnace ensures the minimum surface area with the maximum useful capacity, resulting in low heat radiation and high throughput capacity. A short rotary furnace of the type 30×30 (outside length 3·0 m, outside diameter 3·0 m, useful capacity 2·2 m^3) heated with Bunker coil can treat about 50 tons of battery scrap per day. Oil consumption is about 5–7% of the weight of battery scrap.

The quantity of fluxes required depends on the composition of the battery scrap and the type of fuel. Good results have been obtained with an addition of 1·5–2% pyrite calcine, 1–2% soda, and 1–2% coal. For charges smelted in furnaces fired by pulverized coal, it is advisable to add 2–4% limestone for slagging the silica of the ash.

In the treatment of lead ash containing about 7% lead, the oil consumption amounts to 8–10% of the lead ash input. The corresponding quantities of fluxes are about 5% soda and coal plus about 15% pyrite calcine or iron ore.

The treatment of both battery scrap and lead ash results in slags containing less than 1% Pb which can be directly dumped.

These advantages of the short rotary furnace, i.e. rapid charging, short smelting and reaction time and simple control, make this furnace highly suitable for the treatment of battery scrap, particularly when relatively small amounts of battery scrap are to be treated to obtain antimonial lead for hard lead work and slags which can be directly dumped.

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New Method for Treatment of Waste Pickling Acid

Kiheiji Tamaki

THE composition of waste pickling acid varies with the pickling process adopted i.e. batch operation or continuous operation. It also depends on the quality of steel plates desired after pickling, the local demand-supply situation of sulphuric acid, etc. The recent large-scale pickling machines requiring waste-acid-treatment facilities are often of the continuous type and involve a larger amount of free sulphuric acid than machines of the batch type.

An example of the composition of waste pickling acid (continuous type) is given below :

Specific gravity	1·197	Sb	Trace*
Fe^{+++}	1·03 g/l	Ti	Nil*
Fe^{++}	34·65 g/l	Mo	Nil*
Mn	141·5 mg/l	Co	Nil*
Cr	4·6 mg/l	Al	Nil*
Ni	7·6 mg/l	Zn	Nil*
SO_4^{--}	200·67 g/l	Sn	Nil*
Cl^-	3·88 g/l	Pb	Trace*
Free acid (as H_2SO_4)	137·69 g/l		

The main constituents of waste acid are sulphuric acid as free acid and iron in the form of ferrous sulphate. The waste contains only small quantities of impurities such as metal ion when compared to titanium waste acid, but chlorine ion is sometimes present. An inhibitor is also added to it (1) to reduce the melting loss of steel in pickling (2) to reduce the quantity of sulphuric acid required (3) to obtain smooth surfaces without causing hole erosion (4) to help the acid permeate between iron and the scales on its surface and into intermediate layers, and thus promote pickling.

Various inhibitors are used in different plants, and their composition is often kept secret. However, they are known to consist of an organic compound, containing N.S.O., such as, propa agyl alcohol, quinolines, etc., combined with a surface activator.

Free acid and iron ion contents also vary in different plants, and even in the same plant sulphuric acid changes by 100–200 g/l, Fe^{++} by 30–40 g/l, and Fe^{+++} by 0·4–2·5 g/l.

The composition of coke oven gas varies with the quality of coal feed, the form of the oven, working conditions, and the type of after-treatment. The following is an example of the composition of coke oven gas :

CO_2	1·8– 2·5%	Sulphur H_2S	3·3–5·4	g/Nm^3
CO	6·8– 7·6%	Organic Sulphur	0·2–0·4	,,
CmHn	3·4– 4·2%	Naphthaline	0·013	,,
O_2	0·1– 0·3%	Ammonium	5·4	,,
CH_4	29·9–31·1%	HCN	1·56	,,
N_2	4·2– 6·0%			
H_2	49·5–51·0%	Tar base (as pyridine)	0·45–0·7	,,
		Tar grains about	0·25	,,

The above figures indicate the average composition of the crude coke oven gas (COG) sent through the tar extractor by the blower after it has been brought out of the coke oven and separated from gas liquor (the ammonia liquor mentioned later is produced by separating tar from this gas liquor) by the primary cooler.

Earlier methods

In iron and steel plants using COG as fuel for the open-hearth furnace, heating furnace and soaking pit, the gas is refined by removing its ammonia by pure sulphuric acid, recovering ammonium sulphate at the same time. The possibility of using pickling waste acid instead of sulphuric acid has been studied since the 1930's, and the various processes and patents on this subject are briefly reviewed in the following lines.

F. A. Elzi proposed the conversion of free acid into iron sulphate by treating waste acid with scrap iron, neutralizing it with COG to less than pH 7·5, raising the pH to 8·0–8·5 by the ammonia gas issuing from the ammonia liquor still, and finally precipitating ferric hydroxide for the purpose of separation by blowing air into the liquid at a pH of not less than 8·0. In this method the colloidal precipitate of ferro-hydroxide which forms in the first ammoniation, becomes sticky and dense, thus hindering the subsequent reaction. Furthermore, the ammonium in COG is not completely removed in the neighbourhood of pH 7·5, and after the above treatment neutralization is completed in the saturator by sulphuric acid, thereby increasing the wind pressure on the coke blower. The following drawbacks are also to be mentioned : (1) as it is difficult to achieve perfect oxidation, soluble iron remains ; (2) filtration of precipitate is not satisfactory and the ammonium sulphate recovered from the liquid is tinted, etc.

W. Tiddy and others proposed the following method : Treating waste acid with COG, precipitating and separating the greater part of sulphuric acid as FeS and the

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*Spectrographic qualitative analysis conducted.

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remainder as $Fe(OH)_2$, $(NH_4)_2$ $Fe[Fe(CN)_6]$, diluting the precipitate and iron sulphate by mixing 60 to 90 per cent of the separated liquid with waste acid and accelerating reaction by circulating the mixture. This method is effective to reduce risk of clogging in the reactor or increasing the pressure difference, to reduce precipitation per unit volume of liquid and thus facilitate separation. However, although FeS has a greater filtering efficiency than $Fe(OH)_2$, it is very fine—its filtering efficiency in cake form is 230 kg/m^2 hr. Besides, a pH of not less than 7·0 is necessary to obtain the precipitation of FeS, but in this condition it is impossible to ensure perfect absorption of ammonium

Tiddy and others therefore split the process into two stages—the reactor for the reaction of H_2S, HCN, etc. and the absorber for the absorption of ammonium. For this purpose, a device such as a spray tower with less pressure difference will be necessary considering the burden on the coke blower. In view of the large quantity of COG, a two-stage reactor will be more expensive to build, while circulation of a large quantity of liquid will necessitate a large filter.

Furthermore, as the precipitate includes $Fe(OH)_2$, its colloidal nature may hamper filtration and the subsequent oxidation being incomplete, ammonium sulphate may be coloured.

The precipitate containing FeS and $(NH_4)_2Fe[Fe(CN)_6]$ can hardly be used for production of sulphuric acid due to its water content and even less for direct iron extraction. R.D. Hoak attempted to solve these difficulties : Waste pickling acid is brought in contact with COG and a slurry of ammonium sulphate solution and FeS, Fe_2 $[Fe(CN)_6]$, NH CNS is formed at a pH of 6·2–7·0. At this stage H_2S is not removed completely ; it is removed subsequently by treatment with a slurry of oxidized steel. The FeS of the slurry is turned into Fe_2O_3 and S by oxidizing it at a pH of 6·5–7·5. The solid is then separated from the liquid, and NH_4 CNS is recovered from the liquid while Fe_2O_3 is recovered from the solid by removing ferrocyanide as Ca_2 $[Fe(CN)_6]$ and separating S by flotation. This method, though quite effective, has the following disadvantages : (1) the process is complex and involves heavy constructional expenses ; (2) the quantities of H_2S, NH_3 HCN contained in COG change so much that when H_2S decreases Fe $(OH)_2$ increases, and when NH_3 increases it cannot be completely removed ; (3) the sulphur is likely to become colloidal, making filtration incomplete ; and (4) some of the $(NH_4)_2Fe$ $[Fe(CN)_6]$ contained becomes soluble during the oxidation process and the ammonium sulphate obtained thus gets coloured.

As an improvement on the above process, G.E. Muns and others proposed a method to make a slurry from the precipitation of FeS, $(NH_4)_2Fe$ $[Fe(CN)_6]$ by the reaction of waste acid and COG at a pH of 7·5–7·8, leaving FeS by about 0·2–0·5 per cent to oxidize this slurry, and thus preventing $(NH_4)_2$ $Fe[Fe(CN)_6]$ to become soluble and the ammonium sulphate to become soluble and coloured. However with this method it is first impossible to fully remove NH_3 from the COG at the pH of 7·5–7·8, and when FeS is left over during the oxidation of $FeSO_4$ it would inevitably remain and cause colouring. To solve these difficulties, G.E. Muns and others in 1958, proprosed a method in which waste acid was made to react on COG in two stages : to remove ammonia completely, waste acid was first neutralized with COG at a pH of 3–3·5 and then H_2S, HCN and ferrous salt were made to react on each other at a pH of 7·5–7·8. To refine COG at low cost E.B. Mancke and others proposed in 1958 a method wherein waste acid flows in a continuous line and COG in two parallel lines.

The objective of all these methods is to make the H_2S, HCN of COG react on the iron of the waste acid. They require a two-stage reaction process first to remove the H_2S, HCN of COG and then to completely eliminate NH_3. Removal of H_2S, HCN of COG with waste acid is very attractive if elimination could be complete. According to E. B. Mancke and others, H_2S is removed by less than 1·4 g/Nm^3 (rate of removal : 85%) and HCN by less than 0·23 g/Nm^3 (rate of removal : 50%). Considering the load on the coke blower from the fact that COG must be given a two-tank treatment, it is impossible to have a large pressure difference and this is another reason, why the rate of acid removal will be restricted. The necessity of a two-stage treatment tank and tower entails heavy construction expenses. When precipitating primary ferrous salt in the form of FeS, $(NH_4)_2$ Fe $[Fe(CN)_6]$ by means of H_2S, HCN, it is difficult to completely precipitate the iron as long as solution of $(NH_4)_2$ Fe $[Fe(CN)_6]$ is prevented. Iron sulphate remains and causes colouration of ammonium sulphate.

The precipitate of FeS, $(NH_4)_2$ Fe $[Fe(CN)_6]$ and $Fe(OH)_2$ is very fine and though it is not as fine as the precipate of $Fe(OH)_2$ alone, it is difficult to fllter. Oxidation of slurry containing FeS, $(NH_4)_2$ Fe $[Fe(CN)_6]$ is apt to accompany the formation of biocyanate, and consequently separation of free sulphur is not necessarily very easy. The precipitate consisting mainly of FeS and $(NH_4)_2$ Fe $[Fe(CN)_6]$ is in itself difficult to dispose of and its conversion into Fe_2O_3 will further necessitate a device for separating its ferrocyanide. Such practical drawbacks explain why none of the above processes have been so far adopted by the industry.

Neutralization process, or Fuji Iron and Steel Method

The Fuji Iron and Steel Method does not present the above difficulties. It is a new process ensuring maximum economy in the treatment of waste acid by COG, especially in the continuous pickling tank. The Fuji method aims at the removal of NH_3 from COG instead of H_2S, HCN. Therefore, even if the latter remains it may be used as fuel, and when in very small quantity it may be removed by a separate refining device. The advantages, if any, in decreasing H_2S, HCN may be negligible compared with the ease of disposal of the waste acid at no additional requirement of sulphuric acid to remove the NH_3 of COG.

The reactions taking place, when COG is treated with waste acid, can be represented by :

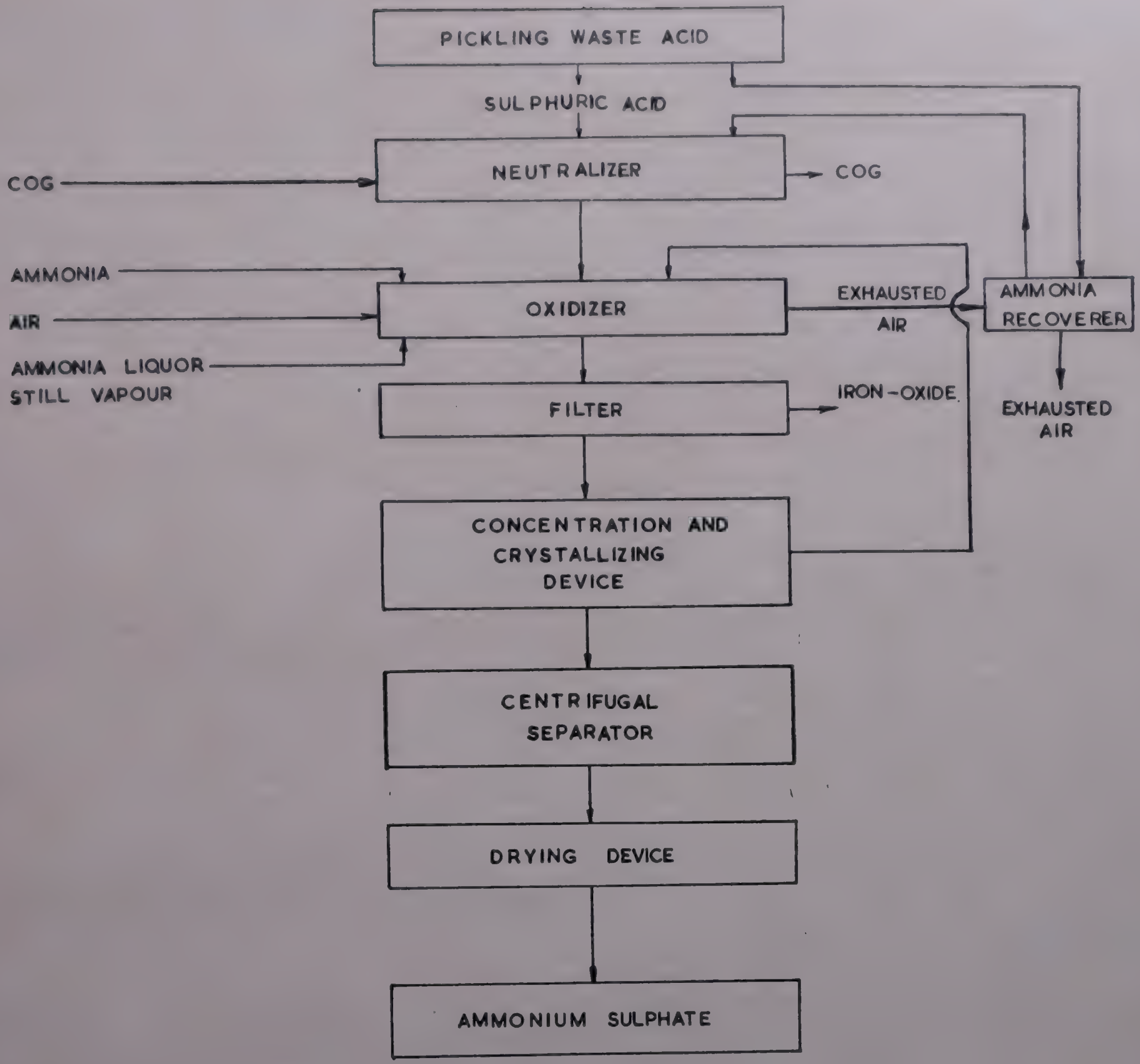
(1) $2NH_3+H_2SO_4=(NH_4)_2\ SO_4$

(2) $6NH_3+3FeSO_4+6HCN=3(NH_4)_2\ SO_4+Fe_2\ Fe(CN)_6$

(3) $2NH_3+FeSO_4+H_2S=(NH_4)_2\ SO_4+FeS$

These reactions are gas-liquid reactions, and the ease with which they can take place depends on the quantity of each gas and degree of solubility. H_2S hardly dissolves in a liquid of pH 3 to 5, while HCN dissolves much more than H_2S though not as much as NH_3.

In the Fuji method, COG is made to pass through waste acid and continuous neutralization takes place at pH 3–5. Under this pH value most of the NH_3 of COG is collected. Although NH_3 is soluble, it does not dissolve to the extent of precipitating $(NH_4)_2$ $Fe[Fe(CN)_6]$ or $Fe_2[Fe(CN)_6]$. This neutralization process has the following advantages : (1) The saturator with which ammonium



1 *Fuji Iron and Steel Process for treatment of waste pickling acid*

sulphate has hitherto been recovered by using new sulphuric acid can be used as such ; (2) Two-stage reaction is not needed ; (3) there is no need for a special absorption tower such as the bubble cap column ; and (4) as the liquid is not saturated it will not get clogged and will ensure continuous neutralization.

The neutralized liquid thus obtained hardly shows any precipitation. It may, therefore, be concluded that the free acid in the waste acid is neutralized and turns into ammonium sulphate, and that ferrous sulphate remains as such. It contains HCN, H_2S to the extent of solubility.

The temperature of the neutralizer is of 40–55°C and depends mainly on the temperature of COG.

The solubility of H_2S for water at 40°C is 0·07 mol/1, and, therefore, $(H^+)^2 (S^{--}) = 0{\cdot}77 \times 10^{-23}$.

Now assuming the density of hydrogen iron as 10^{-3} mol/1, $(S^{--}) = 0{\cdot}77 \times 10^{-17}$. On the other hand, since (Fe^{++}) may be considered equal to 0·6 mol/1, $(Fe^{++})(S^{--}) = 0{\cdot}46 \times 10^{-17}$. The solubility constant of FeS being 4×10^{-19}, FeS ought to precipitate even at a pH of 3. However, the formation of supersaturated solution or a very small crystal shows different solubility product in many cases. In practice, the value of pH varies even in a saturator according to portions from which somples have been taken, but experiments show that no precipitation is detected at a pH of 5. However, there exist $[S^{--}]$ or $[HS^-]$, $[CN^-]$ in proportion to solubility.

In this process, pyridine and other substances in the tar are mostly collected in the neutralized liquid.

The main problem here is to balance the NH_3 content of COG and the free sulphuric acid contained in the waste pickling acids. To make the process more economical it is advisable to increase concentration of free acid in the pickling tank by adding the required amount of sulphuric acid in the pickling tank itself. This would also increase pickling capacity and improve the quality of steel plates.

Sulphuric acid is needed in an ammonium sulphate plant for two purposes : for neutralizing the NH_3 content of COG and for neutralizing the NH_3 obtained by distilling the ammonia liquor still. The former requirement usually accounts for about 70 per cent of the acid. With a waste acid similar in composition to the one mentioned earlier, and if all sulphuric radicals are balanced, free acid would be almost balanced with the NH_3 in COG. Therefore in the case of waste acid from continuous pickling tank, the free acid can be neutralized by the ammonium contained in COG, provided all sulphuric acid radicals are balanced. A slight change in composition is adjusted by using fresh sulphuric acid and synthetic ammonium, but for replenishing NH_3 as mentioned later, it may be more advantageous to send the required quantity of vapour of ammonia liquor still to the neutralizer, and NH_3 to the oxidation process.

It has been established by the Ishihara Industrial Co. (Yokkaichi City, Japan) that the inhibitor in waste acid has adverse effects in subsequent oxidation process, and the firm devised a method to solve this problem and has applied for a patent. However, the most advantageous feature of the Fuji method is that the effect of the inhibitor can almost be avoided by treating waste acid with COG. This is attributed to the fact that the tar grains in COG absorb the inhibitor when they float in the neutralized liquid, or that it is removed by the stripping effect of the gas.

Oxidation process

The neutralized liquid produced by almost neutralizing the free acid during the neutralizing process is oxidized during the same process by air blowing. The iron in the ferrous sulphate is then precipitated in the form of black hydrated ferroso-ferric-oxide (F.F.O.) and the sulphuric acid radical becomes ammonium sulphate. This process is adopted by the Ishihara Industrial Co. for the waste acid of titanium oxide. The ease in filtering the precipitate and the ferric solution in the liquid make this method quite suitable for an industrial scale operation.

The Fuji method is characterized by the simultaneous blow of air and ammonia into ammonium sulphate solution containing ferrous sulphate, dispersing the air as fine bubbles by means of a special stirring device thus oxidizing primary iron into secondary iron. In consideration of the granular formation of the precipitate and its nature, it is advisable to have the ratio between the secondary and primary iron from 2 to 3·5. The separating sulphuric acid is immediately neutralized into ammonium sulphate to prevent fall of pH. The iron is precipitated as F.F.O., in the form of FeO, Fe_2O_3, nH_2O. This molecular formula shows that the value of the ratio of ferric iron to ferrous iron is 2, but the one with a value of 3·5 has larger grains and is quick to precipitate and easy to filter. When it is further oxidized the grains become finer and the precipitation slower. The speed of oxidation changes according to the quantity of air, agitation, pH, temperature, etc.

According to the Ishihara process, synthetic ammonia or ammonia of equal purity is used for neutralization and oxidation. In the Fuji method, the NH_3 of COG is used for neutralization, and, the vapour of ammonia liquor still is used for the oxidation process. As air is also drawn simultaneously in the oxidation process, the NH_3 of COG cannot be utilised. The neutralized liquid contains H_2S and HCN to a saturating extent, and the ammonia liquor vapour also contains sulphides and cyanides. The great advantage is that they are present in much smaller quantities than in COG ; FeS $(NH_4)_2$ Fe [Fe $(CN)_6$], etc., are not easily formed because air is drawn in simultaneously ; in addition to the use of COG in the neutralization process, waste acid can be treated much cheaper than by using synthetic ammonia.

This oxidation reduces the soluble iron content of the liquid to less than 1 mg/l ; the slurry weighed 200 grams, and the time required for filtering it through a funnel of 11 cm diameter was less than 20 seconds at 100 mmHg abs. pressure. A leaf test by filtering cloth showed a filtering efficiency higher than 3000 l/m^2 hr in the case of a 3 mm thick cake.

When pure ammonium is used, NH_3 loss increase even at a pH higher than 7·5, which is advantageous because oxidation becomes quicker.

Use of COG and ammonia liquor vapour quickens oxidation but involves the risk of ferro-cyanide becoming soluble and thiocyanate being generated when the pH is raised to more than 7·8 ; it is therefore desirable to keep the pH lower than 7·8 or possibly lower than 7·6.

If the quantity of ammonia liquor vapour is insufficient with respect to iron sulphate the balance will be maintained, by replenishing pure ammonia.

The separated iron sulphate contains less than 3% sulphur and more than 65% iron, and is therefore suitable as raw material for iron production.

Filtration and concentration processes

The slurry of oxidized liquid is continuously filtered by a suitable vacuum rotary filter. The cake is washed, moisture amounts to 20 to 30%, and the remaining ammonium sulphate 2%.

The degree of clarity of the filtrate, as compared to that of distilled water fixed at 100, amounts to more than 75% when 430 mμ filter is used, and more than 80% wnen using a 500 mμ filter.

The filtrate is concentrated by ammonium sulphate solution by evaporation cans such as the multiple effect evaporiser, and ammonium sulphate crystals are thus obtained.

The quality of ammonium sulphate produced by this process is as follows :

	Ammonium sulphate	Standards laid by Ministry of Agriculture and Forestry, Japan
Ammoniac nitrogen (%)	21·1	20·9
Free sulphuric acid (%)	Not detected	Less than 0·5
Thiocyanate compds. (%)	Not detected	Less than 1·0
Arsenic (%)	Less than 0·02	Less than 0·5

This ammonium sulphate is as white as the synthetic product and far superior in purity and colour to the ammonium sulphate usually obtained by means of saturator at a coke ammonium sulphate plant.

Conclusions

1. This process ensures perfect disposal of the waste pickling acid and thus solves the problem of pollution of waters by such wastes.

2. Iron oxide of sufficiently good quality for iron extraction is produced (depending on the subsequent treatment, it can be used also as pigment) : the ammonium sulphate obtained is equal in quality to synthetic ammonium sulphate and these products are valuable and easy to dispose of.

3. The materials needed for the treatment are COG and ammonia liquor ; small quantities of sulphuric acid and synthetic ammonia may be needed to maintain the balance. The ammonia in the COG is harmful and has to be removed. Ammonia liquor has to be distilled and freed from ammonia, phenol, etc. before it is disposed of. This process therefore covers the cost of treatment and is even profitable at times as it yields ammonium sulphate and iron oxide.

4. This process can be introduced in a coke plant producing ammonium sulphate from sulphuric acid using a saturator. The saturator can be used as a neutralizer and provision must be made for an oxidizer, filter, and concentrating and crystallizing equipment. This is all the more advantageous as it does not interfere with the operation of the coke plant.

5. The pH in the neutralizer is of 3 5 and, it almost shows neutrality after the oxidizer. From the viewpoint of equipment this process is therefore anvantageous when compared to processes which concentrate waste acid as such.

6. The process permits continuous operation ; with the adequate equipment the process can be carried out by few operators.

7. The ammonia in the COG can be completely removed.

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Research and Development Work on the Utilization of Metallurgical Wastes at the National Metallurgical Laboratory

B. R. Nijhawan

RECOVERY and utilization of metallurgical wastes and by-products have essentially so far been "back-yard" in character. Such "back-yard" background of recovery and utilization of metallurgical wastes has so far perhaps been due to earlier abundance of rich ores and requirements of simple end-products and in their wake compound profits—such a situation is hardly tenable today. The general pattern is that metallic ores are gradually becoming leaner whilst the metallurgical properties and characteristics of different metals and their alloys are becoming progressively stringent and critical on the basis of rigid standard specifications and specialized service requirements. The rising production and processing costs thereby necessitate "beneficiation" of overall economics aligned not only to improve upon the intrinsic metal extraction balance sheet but also to maximize the recovery and utilization of process wastes and by-products with the objective of turning them into useful metallurgical and financialassets instead of cumulative disposal liabilities. The role of research and development work in transforming dumps of metallurgical wastes into useful consumer products is not only supreme but also opens out a challenging vista in terms of metallurgical research ingenuity, applications of engineering technology and requirements of consumer's market end-products.

All advanced countries have passed through such metallurgical and economic development phases whilst the developing countries will have to huddle through them at a faster tempo in view of the availability of specialized "know-how" and advancements made in metallurgical and engineering technology. However, any wholesale transplantation of advanced technology on under-developed soils may not fructify. Metallurgical wastes and by-products whilst following a general conventional pattern will possess certain basic characteristics typical of the indigenous starting raw materials. Naturally, therefore, optimum metallurgical techniques for utilization of metallurgical wastes and by-products will have to be chiefly indigenous in character and more so in execution. Furthermore, metallurgical by-products tend to deteriorate in quality in terms of their recoverable values, as the starting ores become increasingly leaner. In the above general pattern of depleting resources and spiralling processing costs, the value of metallurgical research and development work can hardly be underestimated in any country and equally if not more so in India which calls for comprehensive research planning, systematically pursued in close co-ordination with indigenous mineral and metal industries. The National Metallurgical Laboratory realizing the importance of these objectives, started both short term and long range research projects on the following basis :

1. Treatment of mining rejects and mineral discards, such as of ore fines and other low grade by-products—their beneficiation, processing and optimum utilization.
2. Utilization of slags and residues ; treatment of by-products of metal industries, such as of blast furnace and steel slags, flue dusts, millscale, coke breeze, etc.
3. Utilization of drosses, swarfs, skimmings, such as of zinc dross from galvanizing shops, aluminium dross, reclamation of lead and processing of electro-metallurgical residues and muds.
4. Utilization of metallurgical waste gases, such as during electric smelting of ferro-manganese and related fields.
5. Miscellaneous utilization studies, such as of steel scrap reclamation, refractories raw materials etc.
6. Scientific research studies such as relating to mineralogy and slag phase systems based on hot stage microscopy, X-ray diffraction analyses and other physical methods of examination of metallurgical by-products and wastes.

The planning of research on such a wide spectrum calls for an analytical approach in forming priorities and perseverance in its execution. It is today well established that research and development work in these fields can hardly be considered complete in most of its phases—such a yardstick equally applies to the work of National Metallurgical Laboratory in the fields of mineral and metal wastes and by-products and yet results in several themes have indicated clear trends and avenues along which the ultimate solution lies. It is equally encouraging that in some cases, industrial scale implementation of the research results has been readily forthcoming based on the economic acceptability and metallurgical feasibility of the investigations conducted at the National Metallurgical Laboratory. A general outline of the work at the National Metallurgical Laboratory in the above fields will be now given along with current thinking on the subject along which future work is being planned.

Dr B. R. Nijhawan, Director, National Metallurgical Laboratory.

Treatment of mining rejects and mineral discards, such as of ore fines and other low grade by-products—their beneficiation, processing and optimum utilization

Agglomeration of iron ore fine wastes

Mechanized iron ore mining, crushing, and screening release 25–40% of ore fines which have, at one of the Indian ore mines, built an almost artificial hill for posterity's view. In the current analysis, discard of almost half of the iron ore mines as fines constitutes a national waste in the long run as also goes against the policy of conservation of natural resources. Directly it means increased cost of mining. Such tonnages of iron ore fines during the last year of the Third Five Year Plan may amount to 11–12 million tonnes representing a loss of Rs 60 million. The National Metallurgical Laboratory has undertaken both short-term and long range work on the utilization of iron ore fines by sintering, pelletizing, and briquetting. Optimum beneficiation of the ore fines precedes their agglomeration. Research and development work on these modes of agglomeration for utilization of ore fines in the iron and steel industry have been comprehensive in scope and rewarding in their industrial scale acceptance and implementation by the steel industry.

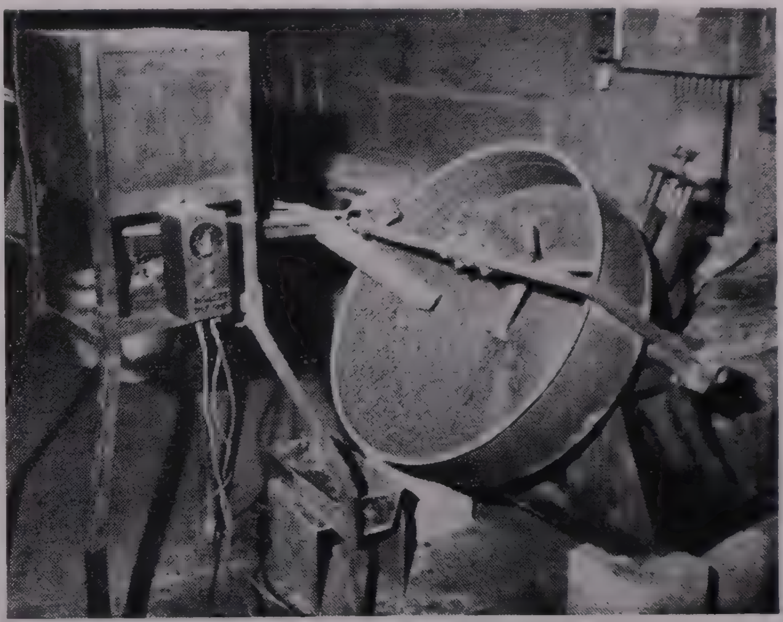
One of the most important methods of utilization of iron ore fines is the use preferably of self-fluxing sinter for ironmaking made out of beneficiated iron ore fines. A good metallurgical sinter can be a perfect agglomerate based on its reducibility, permeability and state of oxidation. All these aspects have been systematically investigated at the National Metallurgical Laboratory for iron ore fines, such as arising at Noamundi, Bolani, Kiriburu, Rajhara, Barsua, etc. ; iron ore mines of steel plants in India belonging to both public and private sectors in India. Several Investigation Reports have been issued by the National Metallurgical Laboratory on the subject. Sintering characteristics of iron ore fines were based on the variables (i) coke or fuel content of the charge which controls the sintering temperature in the bed, (ii) moisture content of the charge which controls the permeability of the bed and thereby the rate of sintering, and (iii) time and mode of initial ignition which determine the overall fuel economy as well as on the sinter quality. Some results of these studies are given in Table I[1]. Furthermore, sintering of iron ore fines enables the utilization of limestone fines, coke breeze, blast furnace flue dusts, mill-scale, etc. which by-products of the steel would be completely wasted.

Another mode of utilization of "blue dust" which has been investigated at the National Metallurgical Laboratory extensively was the successful incorporation of blue dust up to 50% of the sinter mix, composed of washed iron ore fines ($-\frac{3}{8}''$), coke breeze, limestone fines, etc.; yielding a good grade of metallurgical sinter of optimum strength and permeability.[2]

Blast furnace flue dust, an important constituent of sinter, can also be upgraded to over 60% iron by tabling and magnetic separation following a flow sheet worked out at the National Metallurgical Laboratory.[3]

Another mode of agglomeration of iron ore fines such as blue dust is pelletizing – the resultant pellets can be either directly smelted for iron production or exported at a price of 10–12 $ per ton. Specific studies on Goa iron ore fines indicated that after beneficiation of the iron ore fines, strong pellets assaying 66·67% Fe, 2·12% FeO, 2·96% SiO_2, 2·33% Al_2O_3 and 0·05% P could be produced economically which the overseas market could utilize. The hardened pellets could withstand sea transport over extended periods and distances.[4]

1 *Mineral beneficiation pilot plant shed showing the primary and secondary crushing section in the front.*



2 *Disc pelletizer in operation for pelletizing iron ore fines.*

Another mode of utilization of iron ore fines, such as chiefly blue dust is by solid state direct reduction with coke breeze to produce high purity iron powder.

Work done on the above subject is outlined below :

Investigations were initially undertaken in the National Metallurgical Laboratory to study the reduction characteristics of the Indian iron ores for the production of iron powder. Iron powder for flame cutting and scarfing should have a high iron and low oxygen content and possess optimum mesh "size range" consistent with optimum flowability.

India has large deposits of high grade iron ore in which pockets of very fine iron ore known as "blue dust" are met with during mining operations. In Singhbhum-Bonai area about 10% of "blue dust" is obtained during mining.

These iron ore fine lumps are fragile in nature and easily crumble down to iron ore powder. The possibilities of utilizing these ore fines for the production of iron powder were investigated at the National Metallurgical Laboratory and a suitable technical "know-how" has been developed for industrial scale applications.

TABLE I Results of sintering

	Coke %	Water %	Return fines added %	Flux %	Basicity ratio CaO/SiO₂	Rate of sintering, in/min	Return fines made, wt-%	Shatter stability, %	$-\frac{1}{4}$in sinter after shatter, wt-%
Noamundi, Tisco									
1. Unwashed	4	7	20	—	—	0·95	16·8	58·9	6·4
2. Unwashed	4	7	20	13·7 LS and D	2·0 $\frac{CaO+MgO}{SiO_2}$	0·86	16·3	46·1	9·8
3. Washed	4	7	25	—	—	0·68	18·6	64·8	9·7
4. Washed	3·5	7	20	10·2 LS and D	2·0 $\frac{CaO+MgO}{SiO_2}$	0·76	20·4	63·2	9·4
Bolani									
5. Unwashed	4	8	20	—	—	1·13	19·4	52·2	6·8
6. Unwashed	4	8	25	13·2 LS	1·2	1·00	18·6	42·2	9·5
7. Washed	4	7	20	—	—	0·93	20·6	51·8	8·1
8. Washed	3	7	25	10·13 LS	1·2	1·0	21·5	50·1	7·9
9. Washed	3	7	25	7·2 LS 1·8 D	1·3 $\frac{CaO+MgO}{SiO_2}$	0·91	23·5	51·7	9·4
10. Bolani washed and concentrated	4	7	20	—	—	0·73	22·3	55·5	6·0
11. do	3	7	25	7·06 LS Conc.	1·2	0·77	25·3	60·5	6·5
Barsua									
12. Washed	4	7	25	—	—	0·95	22·6	52·6	11·3
13. Washed	4	7	25	13·95 LS	1·6	1·00	17·0	69·6	5·2
14. Washed	4	7	25	4·48 LS 1·49 D	1·3 $\frac{CaO+MgO}{SiO_2}$	0·83	23·4	59·2	8·5
15. Washed and beneficiated	4	7	25	—	—	0·80	24·1	51·2	9·7
16. Washed and beneficiated	4	7	25	6·13 LS	1·2	0·73	17·2	65·5	5·8
Rajhara									
17. Washed	4	7	25	—	—	0·80	24·6	68·1	7·3
18. Washed	3·5	7	25	14·1 LS	1·0	0·90	26·3	59·4	6·6
19. Washed	3·5	7	25	11·1 LS and D	1·0	1·00	25·0	58·1	8·6
20. Washed and beneficiated	4·5	7	25	—	—	0·90	22·0	54·3	5·7
21. Washed and beneficiated	4·0	7	25	12·57 LS and D	1·6	0·82	25·4	61·0	7·3
Kiriburu									
22. Washed	4	7	25	—	—	0·95	18·8	62·9	9·4
23. Washed	3	7	20	10·05 LS	1·4	0·95	21·4	67·7	9·9
24. Washed	3·5	7	20	7·9 LS 2·0 D	1·6 $\frac{CaO+MgO}{SiO_2}$	0·95	18·1	61·7	9·0

LS=Limestone
D=Dolomite

The blue dust lumps being fragile, no grinding was necessary. The blue dust was suitably dried and subjected to solid state reduction at suitable temperature range for optimum period. The reduced powder was most successfully used for flame scarfing and cutting heavy castings of 15% Cr steels exceeding thickness of 10″ dia. in a very short time.

A Project Report for industrial scale production of Iron Powder has been issued by the National Metallurgical Laboratory.

Research and development work at the National Metallurgical Laboratory have established that mill-scale also, an inevitable by-product of steel plants, can be thus reduced to yield the following :

(i) High purity iron powder for autogenous cutting and scarfing which is imported in India today.
(ii) Iron powder for powder metallurgical applications such as bearings, etc.
(iii) For mild steel electrode coating with iron powder containing exceedingly low phosphorus.
(iv) As a catalyst in chemical and textile industries.

Production of high purity sponge iron

There are several direct reduction processes based on the use of solid, oil or gaseous reductants, based on reduction in a fluidized bed, rotary kiln, vertical reaction vessels, etc. These processes are based invariably on the use of heavy capital outlay; under Indian condition, most of them are metallurgically infeasible and economically unacceptable considered in the context of relative lack of gas and oil in natural supplies. In the process developed at the National Metallurgical Laboratory, solid state direct reduction of naturally occurring high grade iron ore fines termed in India as "blue dust" or high grade iron ore ground to optimum mesh size is undertaken. The reductants employed in the NML process is coke breeze which is abundantly available or hard wood charcoal of suitable gradings. The raw materials for direct reduction of rich iron ore fines which cannot be utilized in the blast furnaces are abundant in India and can be well specified for a particular location. The reduced iron pellets prepared by the NML process can be readily employed for the production of high grade alloy, tool and stainless steels—the reduced iron has a purity of iron in excess of 96%. The process is metallurgically feasible and economically fully acceptable.

The raw materials required are: high grade iron ore fines, coke breeze or charcoal and burnt lime. The iron ore fines required for the production of sponge iron should be high grade with a minimum of 66–68% Fe content whilst phosphorus and sulphur contents are low; these ore fines are readily available in India with resources running into millions of tons. The reductants successfully employed at the National Metallurgical Laboratory are coke breeze and hard wood charcoal; the former is readily available in this country.

This solid state direct reduction of iron ore fines by the NML process consists of the following unit operations:

(i) Use of naturally occurring high grade iron ore fines or crushing of the lumpy ore into suitable size for reduction and drying.

(ii) Pelletizing of dry crushed iron ore into suitable form for solid state direct reduction.

(iii) Preparation of the solid reductant—its crushing and drying.

(iv) Packing of the pellets along with the solid reductant in suitable containers.

(v) Heating the packed containers to the reduction temperature and their soaking at the optimum reduction temperature for requisite pre-determined time.

The high grade iron ore in lumps or fines have to be 80%–100 mesh size, fully dried before treatment.

The dried iron ore fines are pelletized with a cheap binder such as molasses (up to 3% with optimum moisture content); the desired pellet size is ½″ to 1″ dia. The green pellets are air-dried or at a temperature below 300°C. The dried pellets have good strength, can well withstand a drop of 6 ft and can withstand handling on belt conveyor system, etc. Pellet's strength criteria both in green and dried state have been worked out.

The dried coke breeze or charcoal or a mixture of the two is crushed to —⅛″ size.

The packing is carried out in metallic or refractory containers of suitable size. Details of container's size etc. have been worked out. The pellets are embedded in the solid reductant ensuring the latter's uniform distribution in the container whose lid is suitably tightly held and closed.

Solid state reduction of the pellets is carried out at an optimum temperature whilst care is taken to see that the containers in the furnace are arranged to ensure uniform heating. The reduction furnace may be gas or oil fired or electrically heated. The reduction of the pellets does not take more than a few hours. The use of molasses as binder is highly advantageous since the pellets thereby contain uniformly distributed organic carbon, which on decomposition promotes the reduction process. The reduction temperature ensures partial sintering of the reduced iron particles. The containers are withdrawn red hot and air cooled.

The reducibility characteristics of a typical iron ore fines sample are given in Table II.

Chemical analyses of the iron ore after crushing

Fe%	SiO_2%	Al_2O_3%	P%	S%
66·9	0·83	1·2	0·041	0·002

1
2
3
4
5
ENGINE DIVIDED

3 *Photograph showing the size and shape of reduced sponge iron pellets produced at National Metallurgical Laboratory from high grade iron ore fines.*

TABLE II Reducibility of the ore using coke breeze as the reductant

Soaking Time	Percentage	Reduction temperature 800 deg.C.	900 deg. C.	1 000 deg.C
4 hours	Fe	11·2	24·5	88·5
	FeO	83·5	21·2	6·1
	C	0·07	0·06	0·11
6 hours	Fe	13·3	86·05	93·7
	FeO	81·1	9·6	1·4
	C	0·08	0·03	0·51
8 hours	Fe	2·9	91·8	96·03
	FeO	75·4	3·44	0·52
	C	0·03	0·86	0·87

At optimum reduction temperatures, the pure iron yield could approach 97% Fe content with less than 0·5% iron oxide.

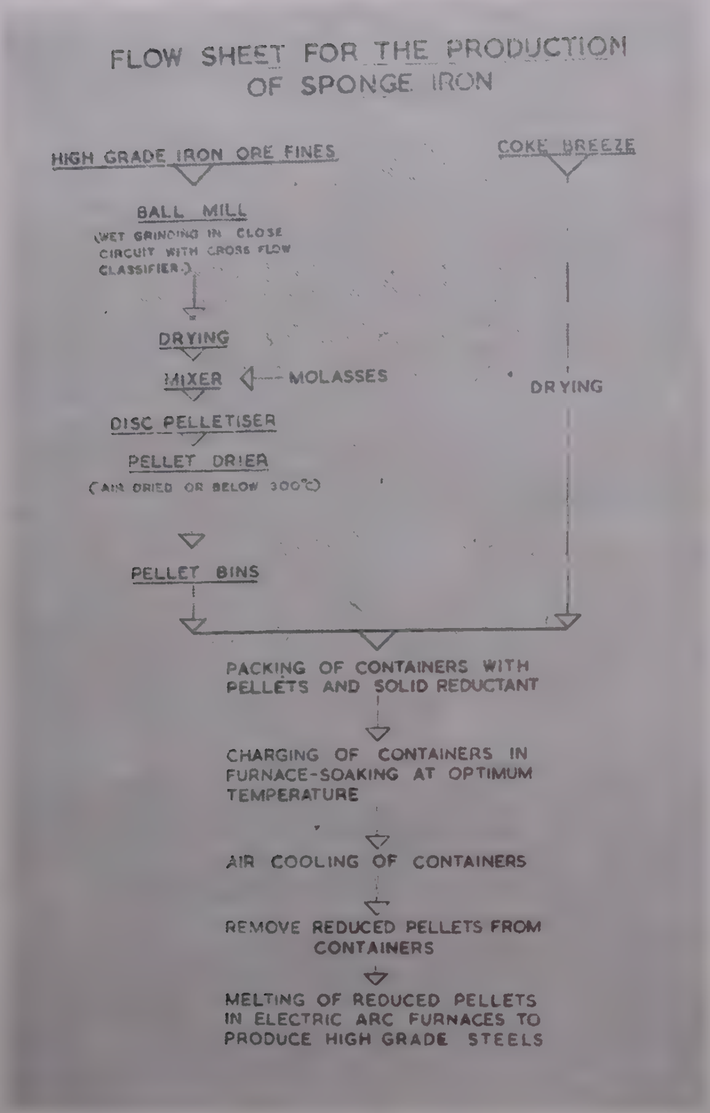
The reduced iron pellets are ideal for use as base for alloy, tool and stainless steel making, which has been successfully undertaken at the National Metallurgical Laboratory.

To prevent any abnormal sulphur pickup from coke breeze, the inclusion of 5% burnt lime to solid reductant is highly satisfactory.

The flow-sheet of the process is given in Fig. 4.

Iron ore fines for the production of sponge iron are of high grade, low in phosphorus and sulphur contents. Naturally occurring high grade iron ore fines are available in India readily. Mild steel, heat resistant alloy or ceramic containers can be employed. Furnace for solid state direct reduction can be gas or oil fired or normal electrically operated. The sponge iron thus prepared is of high purity with an iron content of over 96% and exceptionally low in metalloids. The continuous operation of the process is highly economic and requires exceedingly low capital investment. The entire capital equipment is indigenously available. The process can be operated on a suitable scale to yield 5 000–10 000 tons of reduced sponge iron pellets per year.

Similarly, the utilization of fine grained raw material by briquetting for ferro-manganese smelting has been extensively investigated at the National Metallurgical


FLOW SHEET FOR THE PRODUCTION OF SPONGE IRON
HIGH GRADE IRON ORE FINES
COKE BREEZE
BALL MILL
(WET GRINDING IN CLOSE CIRCUIT WITH CROSS FLOW CLASSIFIER.)
DRYING
MIXER
MOLASSES
DRYING
DISC PELLETISER
PELLET DRIER
(AIR DRIED OR BELOW 300°C)
PELLET BINS
PACKING OF CONTAINERS WITH PELLETS AND SOLID REDUCTANT
CHARGING OF CONTAINERS IN FURNACE-SOAKING AT OPTIMUM TEMPERATURE
AIR COOLING OF CONTAINERS
REMOVE REDUCED PELLETS FROM CONTAINERS
MELTING OF REDUCED PELLETS IN ELECTRIC ARC FURNACES TO PRODUCE HIGH GRADE STEELS

4 *Flow sheet for the production of sponge iron.*

Laboratory. The briquettes could be self-fluxing employing organic binders such as molasses, sulphite lye, etc. The high temperature stability of the briquettes was ensured by the small addition of coking coal of requisite particle size.

Work on the briquetting of iron ore fines was also undertaken chiefly from the angle of export—successful and strong briquettes could be made by the use of a suitable binder.

This work was extended to include coke breeze and limestone dust with inorganic binders such as bentonite for making briquettes whose smelting behaviour was investigated in small blast furnace designed and fabricated at the National Metallurgical Laboratory. Whilst satisfactory grade of pig iron could be smelted, the high fuel and flux consumption and somewhat lower iron yield, the price structure of these waste raw material fines, such as ore fines, coke breeze, limestone dust would determine the economics of iron smelting by briquetted burden.

It would not be possible to discuss all the studies undertaken at the National Metallurgical Laboratory on the subject of by-products primarily through beneficiation. A reference may, however, be made to the recovery of sulphur and gold from tailings from Kolar Gold Fields by suitable benefication technique.

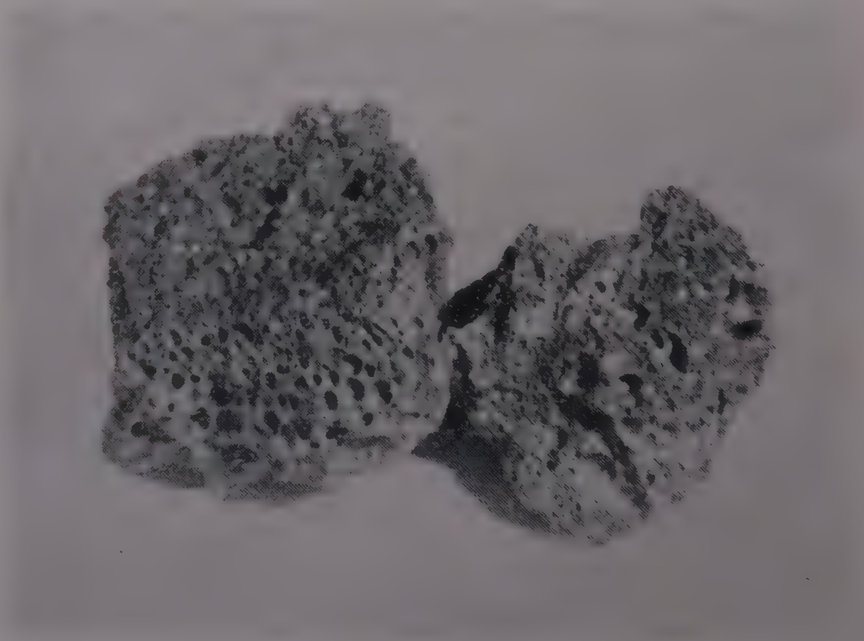
Similarly beneficiation studies on the concentration of uranium bearing tailings from Indian Copper Corporation were undertaken at the National Metallurgical Loboratory. Reference may also be made to beneficiation studies on recovery of ferro-manganese from thes electric smelted ferro manganese National Metallurgical Laboratory.

Utilization of slags and residues ; treatment of by-products of metal industries, such as of blast furnace and steel slags, flue dusts, mill-scale, coke breeze, etc.

Molten blast furnace slags containing low MnO and FeO and high sulphur contents when foamed whilst still at high temperature with a limited quantity of water yield a porous, light and strong product which after crushing and grading, is suitable as coarse and fine aggregate for light weight concrete.

Research investigations on the production of light weight insulation concrete from slags produced at the low shaft furnace pilot plant of the National Metallurgical Laboratory have been undertaken. The physical properties of the slag aggregate made at the National Metallurgical Laboratory conformed to ASTM specifications. Concrete mixes investigated on the basis of volume and weight gave satisfactory unit weight, compressive strength and thermal conductivity values. Concrete with less or "no fine" aggregate gave lower thermal conductivity value, low unit weight and low compressive strength whilst mixes with more fines possessed superior thermal conductivity, greater unit weight and higher compressive strength.[5] In all cases, thermal conductivity value was below 2·0 Btu/(hr.) (sq ft) (F°) (in). The light weight concrete was about 60% lighter than gravel-sand concrete. Thermal conductivity values obtained at different temperatures by Blakely and Cobb apparatus showed a steep rise with increase of the mean temperature.

Recovery and utilization of slags from iron and steel industry cover those obtained from iron blast furnace and steelmaking units. The uses of blast furnace slags are well known, such as for concrete aggregate, bituminous road aggregate, rail ballast, soil conditioners, slag wool, etc. Foamed blast furnace slag provides suitable aggregate for light weight concrete building materials, possessing adequate thermal and accoustic insulation properties. Granulated blast furnace slag finds the well established application of blast furnace slag cement and special mortar. Use of the basic steel slags for fertilizers finds a worldwide application. Recovery of



Expanded low shaft furnace slag lumps.

metallic values from basic steel slag re-cycling in steel melting furnaces is today well established both in India and abroad. Soviet developments in this field include the treatment of molten steel slag with mineral additives for recovery of metallic values and conventional uses.

Similarly, systematic work on the low shaft furnace slags for Portland slag cement has been undertaken at the National Metallurgical Laboratory particularly in relation to higher MgO contents of the slags—the future programme of work covers identical studies on slags containing high MnO content (up to 4%) for Portland blast furnace slag.

The current investigation results have established that the low shaft furnace slag cement used with Portland cement as activators satisfies the requirements of A.S.T.M., B.S. Specifications and Indian Standards Specification in relation to the requirements of chemical composition, compressive strength, tensile strength, setting time, soundness, sulphate resistance of the slag cement, etc. The hydraulicity of the ground slag was evaluated on the basis of its chemical composition in relation to different established formulae and relationships.

Trials were made on the use of iron blast furnace and low shaft slag for coal mine stowing purposes after previously grinding it to requisite fineness. Full scale trials were conducted at a leading coal mine in India in relation to slag, ability to flow characteristics, etc. with the following results :

(*a*) The flow of slag sand through pipes was almost as smooth as the flow of river sand.

(*b*) The quantity of water required to convey the slag sand through pipes from the surface to underground workings was about the same as required for river sand.

(*c*) It appeared that after being deposited underground in the workings, the slag sand made a tighter and more compact bed than the river sand because the percolation of water through this bed of slag sand was definitely less than the percolation through the river sand.

(*d*) On actual weighment, it was found that the slag was lighter than the river sand, the ratio of river sand to slag sand being 1 : 0·763.

Owing to scarcity of good silica sand for coal mine stowing, the utilization of ground granulated blast furnace slag has assumed due importance.

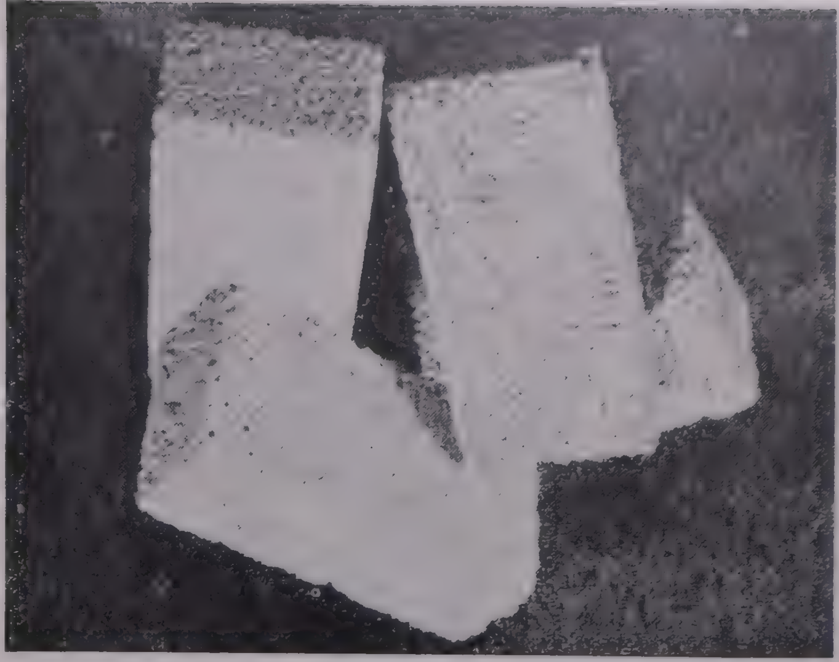
Research and development work at the National Metallurgical Laboratory in steel slags have related to the enrichment of Duplex slag in respect of its P_2O_5 content by the Sylvester process[6].

The application of the Sylvester process for the enrichment of Duplex slag with respect to its P_2O_5 content for the utilization of the enriched slag as a fertiliser has been investigated. Correcting the basicity of the slag to about 2 by the addition of 3 per cent silica to the slag, and firing the mixture at 1350°C. increase its citrate soluble phosphate content from 3·87 per cent to 5·70 per cent. However, the minute crystal size and the intimate interlocking of the constituent minerals hinder the magnetic separation of the phosphate-rich phase of the treated slag.

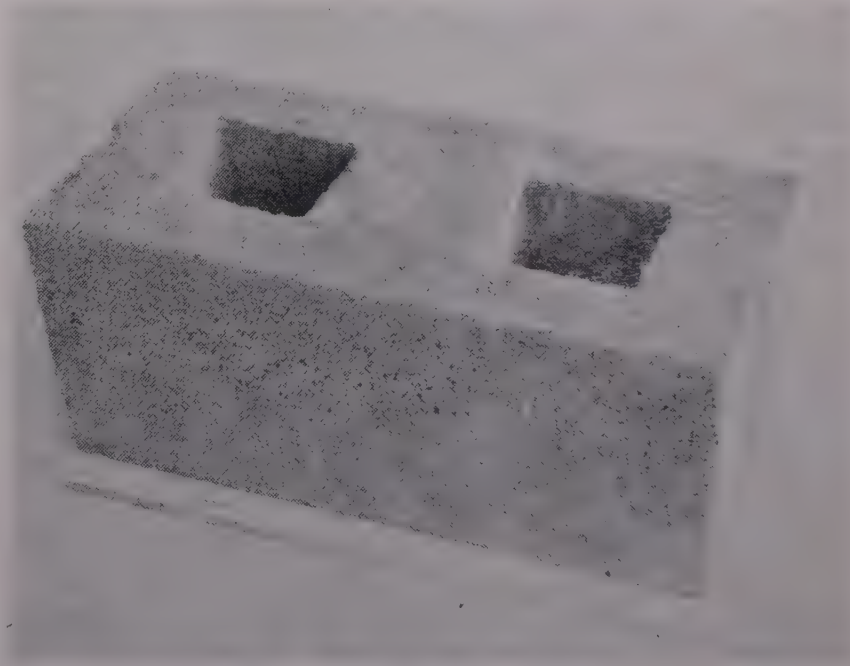
Similarly, the use of beneficiated apatite for the enrichment of soluble P_2O_5 content of Duplex slag for the production of ferro-phosphorus and thermal phosphate was investigated at the National Metallurgical Laboratory[7].

The basic open hearth slag under indigenous conditions of operation runs low in respect of phosphorus content. The utility of basic O.H. slag as a fertiliser depends upon a relatively high P content and its citrate solubility. Likewise the mineral form in which P occurs in rocks renders it useless as a fertiliser and requires the removal of fluorine by calcining the rock in the presence of steam. It was, therefore, contemplated whether a combination of the two indigenous resources would yield a more useful and marketable material. Naturally occurring apatite was beneficiated in the first instance which treatment increased its P_2O_5 content to 37·7% and the beneficiated apatite was added to Duplex slag in a 17 KVA indirect arc rocking type furnace for producing a slag rich in citrate soluble phosphate. It was observed that though the phosphate content of the slag was increased, its citrate solubility was not improved.

The basic O.H. slag was also found unsuitable for the manufacture of ferro-phosphorus in the same indirect arc furnace by the reduction of the phosphate



6 *Light weight concrete bricks and slabs made from expanded low shaft furnace slag aggregate and cement.*



7 *Light weight concrete hollow blocks made from expanded low shaft furnace slag aggregate and cement.*

bearing material with coke and ferro-silicon due to the loss of P by volatilisation.

The suitability of the slag for making thermal phosphate (a smelted mixture of beneficiated apatite with either serpentine rock or serpentine rock and silica, after removal of fluorides by granulating the molten slag with steam) by smelting in the arc furnace was also studied. Investigations carried out with serpentine and silica additions to basic open hearth slag showed that on an average 70% of the available P_2O_5 in the slag was soluble in citric acid, and that this solubility increased with increase in MgO content of the slag.

Utilization of ferro-manganese slag was also taken up with a view to recovering manganese from high-carbon ferro-manganese slag. Investigation was carried[8] out employing ferro-silicon (89 per cent Si) for silicothermal reduction of the slag producing silico-manganese. It was observed that a considerable part of ferrosilicon oxidized during melting and as such further experiments were carried out to minimize the oxidation of ferro-silicon by adopting suitable methods. Studies are also in progress for the production of carbon-free silico-manganese by employing aluminium as a reductant. Systematic studies were also undertaken to investigate the possibility of recovering manganese values from the slag by leaching with sulphuric acid.

Utilization of drosses, swarfs, skimmings, such as of zinc dross from galvanizing shops, aluminium dross, reclamation of lead and processing of electro-metallurgical residues and muds

Work on the reclamation of drosses and related residues from metallurgical shops has received due attention at the National Metallurgical Laboratory. Over 50% of zinc values in galvanizing shops are lost in the form of dross, skimmings, ashes, etc. estimated at 24%, 12–13%, 2–3% respectively. Zinc dross lies at the bottom of the galvanizing bath and by effective operational control can be brought down to 10% of zinc. Chemical analyses of these by-products are given below :

Constituents	Zinc dross	Zinc ash	Zinc skimmings	Zinc blowings
NH_4Cl	—	2·1	10·5	Trace
$ZnCl_2$	—	19·9	34·7	0·5
ZnO	1·7	41.7	34·3	29·0
Total Fe	2·9	0·3	0·5	0·2
L.O.I (at 110°C)	—	2·8	4·4	0·1
Pb	0·5	0·4	Trace	0·7
Zn	94·9	32·6	9·0	68·7

The feasibility of recovering zinc from the dross by distillation at atmospheric pressure has been investigated at the National Metallurgical Laboratory for adoption on a commercial scale. Laboratory scale experiments have established a good recovery of zinc with high purity. Operational factors, such as the temperature of distillation, rate of distillation, inclination of the condenser, material of lining, lining thickness, zone of condensation and its diameter, etc. have been studied. Losses such as zinc dust and zinc oxide were totally eliminated by suitably modifying the condensing system. The new design incorporates certain modifications whereby the condensate is collected in a liquid form by bubbling it through a pool of molten zinc maintained at 450 and 600°C. A recovery value of 95% zinc has been so far recorded and the pure product contains less than 0·04% lead and 0·0028% Fe.

It is proposed to recover zinc from zinc ash and zinc blowings by low pressure and temperature distillation in suitable containers having suitable condensers for deposition of pure zinc vapours in solid form ; the waste products will be pretreated for the removal of other low volatile contaminants. Flux skimmings may likewise be suitably treated in order to find use again as fluxing material.

The sweating process for recovery of zinc from dross was also investigated at the National Metallurgical Laboratory as also the method known as "modified" process[9]. In the sweating process the dross was allowed to sweat at 500–520°C for 2 hours when the higher density iron-zinc alloy settled down at the bottom and the liberated zinc floating on the top was ladled out and cast into an ingot. A recovery of 25% zinc was obtained. The aluminium process which depended upon the greater alloy forming affinity of iron with aluminium than with zinc gave a recovery of 50% Zn. In the modified aluminium process, zinc is separated from the iron-aluminium alloy by taking advantage of the variation in the solubility of zinc in molten lead. Recovery of zinc by this method was 75–80%. The zinc recovered by the modified aluminium process can be reused in galvanising operations. Of the three processes investigated, the aluminium process and the modified aluminium method, employing lead bath separation, merit consideration for the recovery of zinc from dross when zinc is in short supply and provided the price difference between zinc and dross is appreciable.

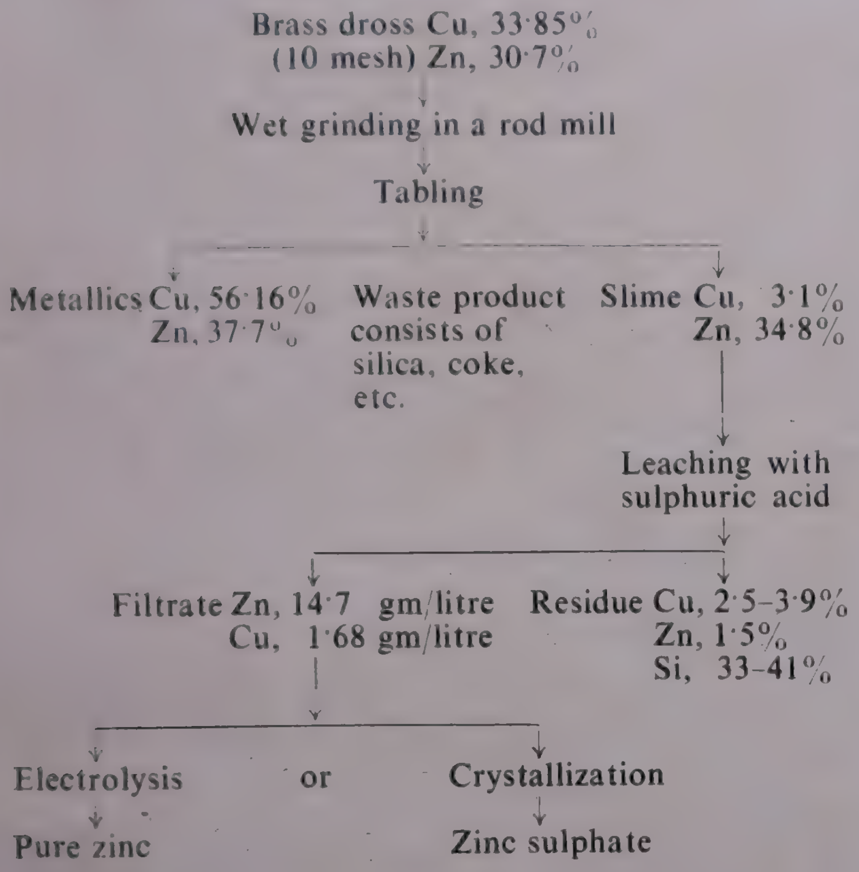
Aluminium foundry dross is associated with metallic particles, metallic and non-metallic oxides, floor sweepings, flux materials, etc. Coarse metal particles can be hand-picked whilst the fines go to waste. The recovery of the metallic values from the dross and other wastes is universally done overseas. It is not economical to recover metallics by direct melting owing to heavy gangue content of the dross and oxidation losses. Dross containing 49% Al could be upgraded to about 80% aluminium by wet grinding in the presence of small quantities of chromic acid to freshly exposed surface of the metal—acid treatment further improves the grade of the metal by preferentially dissolving the alumina[10]. Metallics left in the tailings can be recovered as aluminium chloride, sulphate or nitrate by suitable treatment. The final metal contained Al—84·8%, Al_2O_3—2·98%, SiO_2—5·20%, Fe—2·47%, Si—0·94%, Cu—2·4% and C—0·34%.

Brass dross

Industrial brass dross investigated contained 34·93% copper, 34·5% Zn, 7·49% SiO_2, 1·63% Pb and 1·35% Fe. A simple process of wet grinding to liberate the adherent oxides and washing with water, gave the metallics a content 56·16% Cu, 37·7% Zn whilst the slime contained 34·5% Zn, 3·1% Cu—the latter was leached with dilute H_2SO_4. The flow sheet of the process is given in page 57.

Work on the recovery of copper from scrap was undertaken on the basis of fire refining and electrolytic refining—the subject is of importance in view of the acute shortage of copper in the country.[11]

Similarly some work on the recovery of lead and zinc from flue dust was undertaken—the latter contained 23·5% Pb, 23·5% Zn, 3·0% Cu, 7·8% Fe and acid insolubles 6·7% besides some alumina, chlorine, sulphur and oxygen. The processing covered HCl extraction of the flue dusts yielding a recovery of 80% Pb and 75% Zn.



Lead bullion made from spent bullet cores and scrap secondary lead with total impurities content of 2–3% was investigated for refining to the purity of 99·9% lead. The blended lead blocks were successively subjected to high temperature mechanical drossing with sulphur and softening operation by air to chiefly reduce copper and tin to less than 0·04% respectively as copper renders the lead electrode passive while tin gets co-deposited with lead. After drossing and softening treatment lead was melted and cast into slabs for use as anode with stainless steel plate as cathode, in an electrolytic cell where a mixture of calculated amount of fluo-silicic acid and lead carbonate is used as electrolyte. On electrolysing under optimum conditions at 32°C, ±1°C, 99·97% pure lead was deposited on cathode, which ultimately is used as cathode itself for continuous operation, in place of stainless steel cathode.

Zinc can be electrolytically recovered from almost all types of wastes consisting of zinc compounds. There are several methods available—the one investigated at the National Metallurgical Laboratory[12] on treatment of zinc ash was based on the electrolysis of alkaline (zincate bath) and related to optimum condition for leaching with NaOH for maximum recovery and optimum conditions needed for electrolysis of the resulting zincate bath. The leaching was done with NaOH (400 gm/l) at 90°C for 3 hours to get zinc of 93% purity. Optimum results were obtained when electrolysis was conducted with a current density of 450 amps/m^2 (C.E. of 96·6%) corresponding to a concentration of electrolyte of 40 gm/l and 180 gm/l of NaOH. The zinc thus electrolytically deposited analysed 91·71% total Zn and 79·21% metallic zinc.

Utilization of red mud

Large quantities of red mud are currently dumped to waste at aluminium production plants in India, 0·25 to 0·3 ton of red mud is produced per ton of bauxite treated. The recovery of aluminium, titanium, iron and vanadium oxides as by-products from this easily friable, finely divided red mud should greatly improve the overall economics of aluminium production. Investigations were conducted on the recovery of alumina values from a red mud sample containing 21·4% Al_2O_3, 48% SiO_2, 20·8% Fe_2O_3, 28·8% TiO_2 and 1·8% CaO by soda ash and limestone roasting.[13] Roasting was carried out with soda ash so that 1 mole each of Na_2O was provided for Fe_2O_3 and TiO_2 and the molar ratio of Na_2O_3 was varied. A recovery of only 91% Al_2O_3 was recorded even after increasing the Na_2O_3 : Al_2O_3 as 4 : 1. About 80% of the vanadium in red mud (0·08%) was rendered soluble during roasting and entered the solution as sodium vanadate. At low temperatures, when the liquor contained vanadium around 0·1%, vanadium crystallized out into a complex salt from which vanadium can be recovered ; investigations are underway at the National Metallurgical Laboratory on the recovery of vanadium from such complex salts.

Utilization of metallurgical waste gases, such as during electric smelting of ferro-manganese and related fields

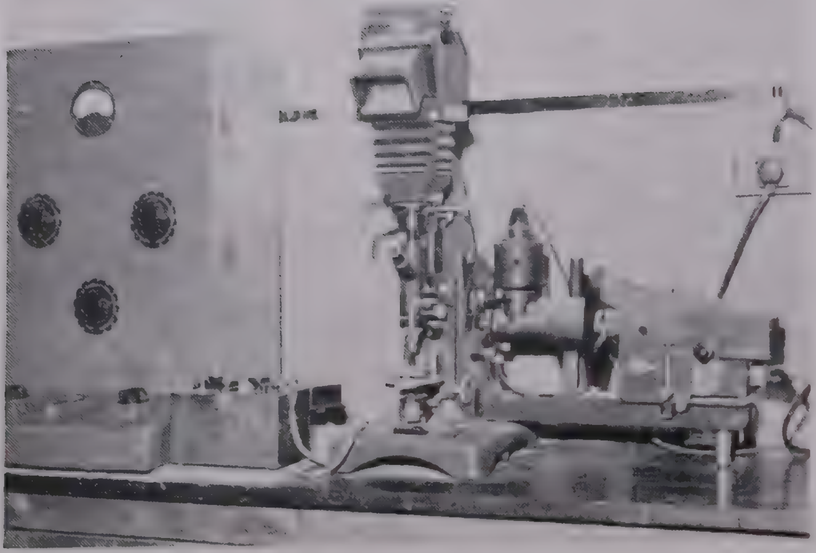
The utilization of waste industrial gases is a vast subject on which considerable work has been done the world over. The subject is complex and can be divided into two categories (*a*) for using the gases for the production of acid, such as H_2SO_4 from SO_2 flue gases and (*b*) for utilizing the gas after cleaning for at site treatment, for upgrading the ore, such as in the case of low-grade manganese ore. The National Metallurgical Laboratory has undertaken extensive research and development work on the magnetizing reduction roast treatment of low grade ferruginous manganese ores based on the use of gas for reduction, such as would be readily available at a ferro-manganese electric smelting unit after cleaning. A pilot plant for beneficiation of low grade ferruginous manganese ore has been set up at the National Metallurgical Laboratory which will employ a synthetic gas of the composition ferro-manganese electric smelting unit normally releases. The pilot plant has been set up at a total cost of Rs 5 million for the Third Five Year Plan.

Likewise, clean low shaft furnace gas with a calorific value 1 350 K Cal/cu m is proposed to be injected into another small blast furnace designed and fabricated at the National Metallurgical Laboratory with or without oxygen enrichment of the air blast—these are some of the Projects on which the National Metallurgical Laboratory would be concentrating.

The injection of surplus light naphtha into the low shaft furnace is another Project on which the National Metallurgical Laboratory would be shortly undertaking pilot plant trials with or without and oxygenated air blast.

Miscellaneous utilization studies, such as of steel scrap reclamation, refractories raw materials, etc.

It has been stated that in the past steel scrap was exported for various reasons—the situation has now considerably changed. Yet the subject of scrap utilization at home is one which calls for development work on the subject. Scrap may be exported at a low price of over Rs 100 per ton and then it returns in the form of finished steel products at over ten times that price structure.



8 *A general view of the hot stage microscopy set up at the National Metallurgical Laboratory.*

9 *A view of the heating cell and the thermocouple in the hot stage microscopy set up.*

There is a good scope for the installation of hot blast cupola for using almost 100% steel scrap for its conversion into iron and steel products. Although steel scraps represent a universal product, the subject almost invariably recedes into the background. The National Metallurgical Laboratory has designed and fabricated a hot blast shaft furnace for melting iron and steel scrap charges and another hot blast cupola of the latest design is now under installation.

There are other 'miscellaneous fields of metallurgical wastes' utilization on which the National Metallurgical Laboratory has undertaken short term investigations, which would relate to the utilization of low grade chrome ores for making high grade chrome-magnesite refractories, processing of sub-standard coarse bladed kyanite for making good quality refractories as also for the light weight highly porous insulation refractories for hot face applications. Likewise, development work on the use of indigenous amphibole variety of asbestos was successfully investigated for diverse applications, such as insulation boards and blocks, etc.

Another important subject on which National Metallurgical Laboratory undertook work related to the reconditioned magnesium powder which had oxidized heavily during storage. Development work relating to the reclamation of used foundry sands through simple flow sheets was another short range project for the industry.

Recovery of pyrites from coal washery rejects through beneficiation techniques yielded a concentrate containing 44·0% sulphur which could be improved to 60% sulphur by using multi-compartment jigs whilst the rejects initially contained 6·3% pyrites sulphur only. The method employed was based on gravity treatment of the coal washery rejects.

Another short range project related to the separation of cryolite from carbon dust from aluminium reduction cells. The upgrading treatment employed was based on agglomerate tabling tests, electro-magnetic separation and flotation. There are also other projects, such as recovery of metallics from gun metal ash by suitable methods investigated at the National Metallurgical Laboratory but it would be difficult to touch upon all the investigations undertaken.

These short term and long range projects as diverse in their scope as these are complex, have been investigated at the National Metallurgical Laboratory—the industrial scale utilization of the research and development work has been forthcoming to no small measure. It is emphasized at the same time that laboratory scale researches and pilot plant trials can only be adjudged in respect of their ultimate merits, by the industry on the basis of their economics and metallurgical feasibility.

Scientific research studies such as relating to mineralogy and slag phase systems based on hot stage microscopy, X-ray diffraction analyses and other physical methods of examination of metallurgical by-products and wastes

In the pursuit of the applied research projects, it has been necessary in most cases to conduct *pari passu* scientific studies with modern research tools, such as hot stage microscopy, x-ray diffraction studies and other physical mehods of examination. Research techniques themselves in these fields are well known, the ingenuity lies in interpretation of the research results and their critical study in relation to their implications. Hot stage microscopy has provided indeed an exceedingly useful technique for mineralogical studies and liquidus determination of the iron low shaft furnace slags. The liquidus temperature of these slags were determined and compared with their calculated values. Different ternary and quarternary slag systems are under study with a view to corelate low shaft slag compositions with their liquidus temperature, viscosity values, etc. The equipment used and some results obtained have been discussed in the NML Technical Journal from which some photographs are reproduced here.[14] The hot stage movie taken by this method showing the formation of different mineralogical phases and crystals has been of great value to the work of National Metallurgical Laboratory in these fields.

The foregoing provides a general review of the research and development work underway and that projected at the National Metallurgical Laboratory in the wide field of utilization of metallurgical wastes and by-products. The research and pilot plant results have to be implemented on industrial scale. Overall economics of waste recoveries and their utilization have to be established and demonstrated in their overall balance sheet. The task is not easy and is certainly not without its pitfalls and breaks and yet the results have been amply rewarding. The overall scope of work is fascinating in all its phases, planning, execution and ultimate assessment in terms of economic acceptance and metallurgical feasibility on the industrial scale, placing indeed a high premium on metallurgical research originality and ingenuity. In these multitudinous tasks, complex yet satisfying, challenging yet rewarding, the young National Metallurgical Laboratory is wholly geared today in answering the call of mineral and metal industries in diverse fields of recovery and reclamation of metallurgical wastes and in its total dedication to the tasks ahead; to prove, if a proof is indeed needed, that the role of research in industry is not only supreme but altogether dominant if not totally indispensable in our country today.

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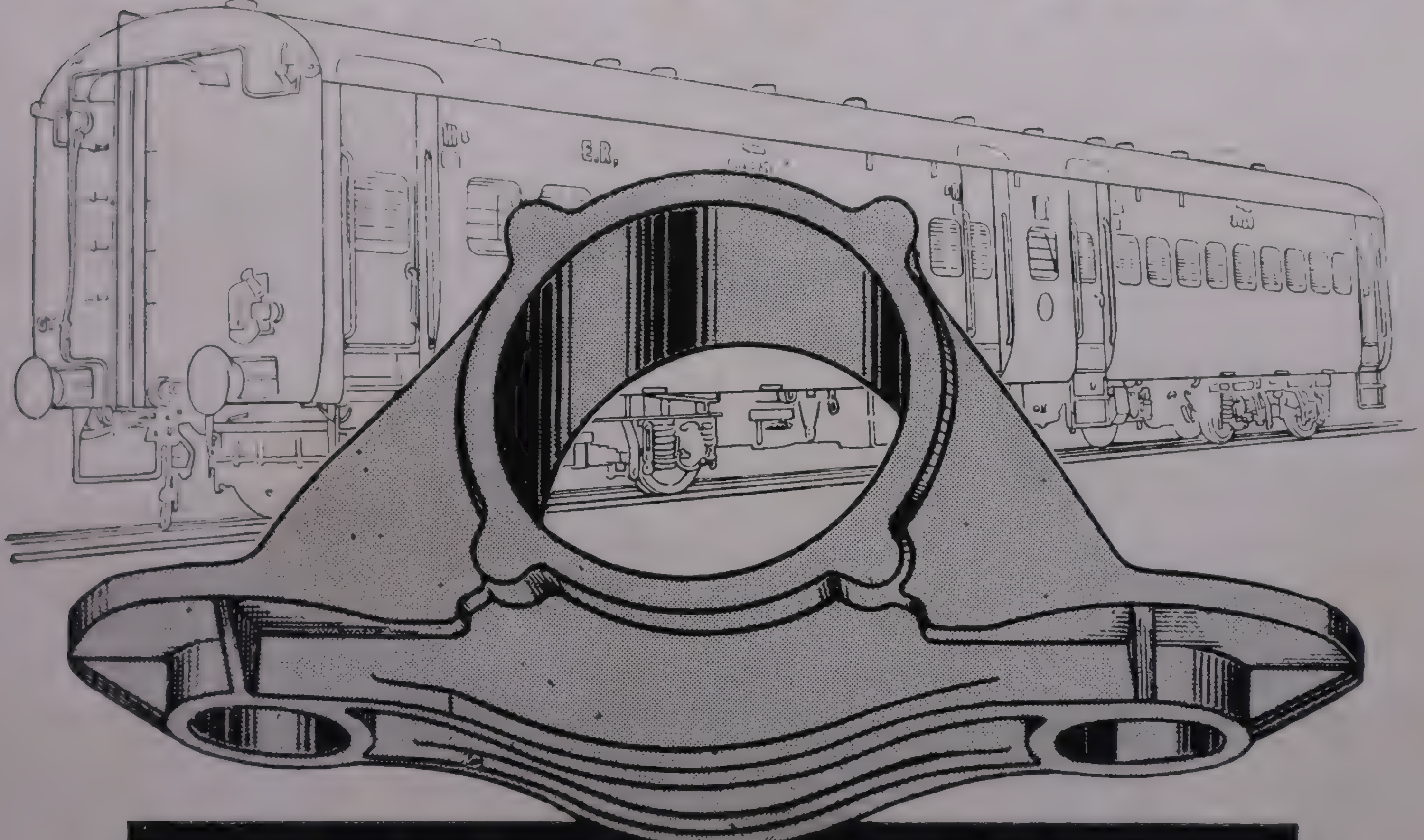

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In Memorium

Members of staff of National Metallurgical Laboratory and their families have been stunned by the sudden passing away of our respected Prime Minister Shri Jawaharlal Nehru and send their respectful heart-felt condolence to Mrs. Indira Gandhi and to all our countrymen. It is much more than a personal loss, even far more than a national loss—it is the loss to the world of a foremost world hero and statesman. Whilst our hearts stand still and world history turns a leaf, we bow to the Almighty Unknown in fervent prayer to lift us from our deep sorrow, mental anguish and intense grief, to dedicate ourselves to our tasks ahead as Indians first and last and to be worthy of being Indians—an ideal which our beloved Prime Minister, Shri Jawaharlal Nehru projected across the span of Indian history. We pay our sincere homage to him and to his ideals—the national pride and patriotic fervour he aroused in Indian hearts are timeless and will glow ageless with us for all times. History whispers, the world is hushed and time stands still whilst we breathe deeply of Shri Jawaharlal Nehru's ideals, even if he breathes with us no more. In the sacred leaves of the Bhagvad Gita, one finds solace in the true significance of life, in the superficiality of physical remains and their inevitable mingling in the dust of nature and silent flow of the Ganges.

The memorable light is out and yet the light in memorium will shine with us for ever, guiding us, leading us on to feel the strength and true pride of being Indians and in dedicating ourselves to the task of building our India, Nehru's India, in our respective domains.

May God give us the strength to do so and grant eternal peace to the noble departed soul. Jai Hind.

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Metallurgical Wastes

THE wasteful discard of different metallurgical wastes and by-products is an economic loss. The utilisation of metallurgical wastes is, therefore, most necessary to 'beneficiate' the economics of metallurgical operations as also to obtain maximum metallic recoveries in the face of depleting mineral resources and increasingly competitive buyer's market. The utilisation of metallurgical wastes has generally been backward, half-heartedly undertaken in the 'back yard' by the metallurgical 'back room' boys ; more so, in India where the metallurgical industries have operated so far on the basis of seller's market. The general apathy towards economic utilisation of metallurgical wastes is now lifting under the tempo of our successive Five Year Plans and in the wake of research and development work undertaken at the National Metallurgical Laboratory. In the same context, the Symposium on 'Utilisation of metallurgical wastes' recently organized by the National Metallurgical Laboratory was most opportune and equally significant in many ways.

Thirty-seven technical papers covering diverse aspects of research and development work on the utilisation of metallurgical wastes, their commercial utilisation, were presented and discussed during the four-day NML Symposium held during the middle of March last.

In this issue of the NML Technical Journal, a brief review of the NML Symposium proceedings has been given. The Symposium attracted distinguished scientists and metallurgists from home and many parts of the world. The Symposium proceedings will shortly be published containing all the technical papers presented and discussed during the memorable NML Symposium week enjoyed by the hosts and the guests alike.

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Symposium on Utilisation of Metallurgical Wastes—A Review

J. E. Mannar
V. Muthukrishnan

THE control of industrial wastes is a problem of great significance, a proper solution of which involves economic, technical and legal factors. The phenomenal growth of metallurgical industries and the rate at which the world's natural resources are being exhausted can be visualised from the fact that consumption of minerals and metals in the last half a century has exceeded what has been consumed in the previous 200 years. The rapid depletion of essential raw materials affects the industrialised countries much more than the relatively under-developed countries. From the standpoint of farsighted national economy, it is essential to conserve and efficiently utilise the raw materials and manufactured products including by-products. Large scale expansion of industrial and mobilisation programmes continues to create critical shortages of various raw materials and brings into play the crucial role of the so-called waste material. The strategic importance of the use of waste products is forcibly brought up during times of war when the drive for self-sufficiency is of paramount importance.

Scope of the Symposium

While the smelting of ores has always received the metallurgical limelight, utilisation of metallurgical wastes has always been 'backyard' in character and scope and yet the basis of overall economics of metallurgical smelting operations rests squarely on the latter. In various metallurgical treatments, by-products and wastes inevitably result. The scope of utilisation of metallurgical wastes is as vast as it is challenging when examined in the context of utilisation of liberated industrial gases, spent pickle liquors, flue-dusts, slime, ore tailings, slags, swarfs, skimmings, residues, ashes, drosses, etc.

The flue dust along with iron ore fines and millscale is used in sintering plants. One of the greatest waste products of metallurgical operations is slag. A number of applications has been developed for utilising slag. Slag is being used at a rate exceeding the production and so recourse is taken to dig into old dumps. The use of slag in the manufacture of cement and as an aggregate for concrete and in civil construction is well established. Slag is also being used for the manufacture of an insulating material known as 'slag wool' and also as light weight aggregates. It has also been used in making glass and steel slag as a fertiliser.

The satisfactory disposal of effluents from the steel plants pickle liquor has plagued the industry for generations. Pickle liquor disposal has been tackled for over 50 years to find a technically and economically satisfactory solution. Apart from recovering usable by-products by the industries, the problem of preventing stream pollution has received great attention from the public health agencies and industries alike. Although promising processes have been developed from the technical standpoint, we have still a long way to go to say that this problem has been satisfactorily solved.

The non-ferrous metals smelting industries too are accompanied by a great waste of by-products. These include the enormous quantity of sulphur that goes out in exit gases. A determined attack to stop the economic loss to the industry and the damage done to agriculture and forestry has at last been solved, so that the recovery of sulphur has added immeasurably to the world's supply of this product. Many lesser known metals such as cadmium and rare earth elements are being recovered from smelter slimes.

Under the tempo of successive Five Year Development Plans in India, primary ferrous and non-ferrous metallurgical industries and secondary processing plants are being progressively set up. However, adequate attention towards effective utilisation of metallurgical by-products and wastes has not been paid so far. It was therefore considered necessary to focus attention on the utilisation of metallurgical wastes particularly under Indian conditions and processing facilities. With a view to focus attention on multitudinous aspects of recovery of by-products and metallurgical wastes, an international symposium on 'Utilisation of Metallurgical Wastes' was organised by the National Metallurgical Laboratory from 10th to 13th March, 1964, to exchange technical 'know-how', examine inter-related problems and discuss effective utilisation of metallurgical wastes along scientific and economic lines.

Inauguration

The Symposium drew a large gathering and more than 200 delegates from all over the world including top ranking scientists and technologists participated in its deliberations.

The Symposium was inaugurated by Prof. Humayun Kabir, Union Minister for Petroleum and Chemicals. Sir Jehangir Ghandy, Chairman, Executive Council, National Metallurgical Laboratory, presided at the function.

Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, in welcoming the delegates from India and abroad, said that such International Symposia offer stimulation of thought and provide an ideal forum for

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Mr J. E. Mannar, Senior Scientific Officer and Mr V. Muthukrishnan, Senior Scientific Assistant, National Metallurgical Laboratory, Jamshedpur.

Prof. Humayun Kabir, Union Minister for Petroleum and Chemicals, delivering the inaugural address at the Symposium. Seated at his left is Sir Jehangir Ghandy, Chairman of the Executive Council of the National Metallurgical Laboratory

exchange of technical 'know-how' and 'know-why' of diverse aspects of the subject.

Dr Nijhawan pointed out that extractive metallurgical techniques are aligned to meet the exacting requirements of not only obtaining maximum metallic recoveries but also of ensuring maximum utilisation of resulting by-products and metallurgical wastes. Such metallurgical by-products tended to deteriorate in quality in terms of their recoverable values, more so, as the basic ores become increasingly leaner. Such a situation was particularly pronounced and equally significant in India since optimum metallurgical techniques for the utilisation of metallurgical wastes in India would have to be basically indigenous in character and execution. As such, the metallurgical wastes and by-products whilst following a general established pattern did pose certain characteristic features typical of the indigenous starting raw materials and processes. These developments, Dr Nijhawan said, would require assessment of metallurgical wastes resulting during the extraction of metals and fabrication of finished end-products in the studies of which the National Metallurgical Laboratory had been actively engaged for several years besides undertaking what may be termed 'technological audit' of metallurgical techniques.

Sir Jehangir Ghandy, Chairman, Executive Council of the National Metallurgical Laboratory, said that in the wake of latest advances in scientific research and technology, many processes had been developed to utilise economically the waste products or the by-products. The National Metallurgical Laboratory, he added, had done exceedingly valuable work on the utilisation of metallurgical wastes, e.g. mine discard like iron ore fines, the recovery of zinc from dross and related non-ferrous fields, etc. Sir Jehangir extended on behalf of the Executive Council of the National Metallurgical Laboratory, their sincere thanks and deep appreciation to Dr B. R. Nijhawan, Director, National Metallurgical Laboratory and his colleagues for the valuable research and development work being done by them and also for the adequate arrangements made for the Symposium.

Inaugurating the Symposium, Prof. Humayun Kabir, Union Minister for Petroleum and Chemicals, said that the response to the Symposium was, in more than one sense, a recognition of the splendid research work the National Metallurgical Laboratory had undertaken within a relatively short span of life. The credit for this would undoubtedly go to Dr B. R. Nijhawan, Director of the National Metallurgical Laboratory and his colleagues who could all take due pride in the Laboratory's achievements. He further paid his compliments to Sir Jehangir Ghandy, Chairman, Executive Council, National Metallurgical Laboratory, for his active support to the Laboratory.

Continuing, Prof. Kabir said that with the development of metallurgical industries and secondary processing plants under the successive Five Year Plans, it had become essential to focus attention on the optimum utilisation of various metallurgical wastes. The major task before the mineral and metal industries today was to utilise to the fullest possible extent their different by-products and waste materials. In the industrially developed countries during the last fifty years, the major advances had been linked with the effective utilisation of possibly all the by-products. The utilisation and exploitation of metallurgical wastes and by-products presented a challenge to the Indian metallurgists and scientists and in this task the National Metallurgical Laboratory had already played and would continue to play a very important role.

Prof. Kabir illustrated the utilisation of metallurgical by-products by the example of the once heavily surplus molasses in India which today are exceedingly in short supply owing to the multitude of applications and also to the once waste and surplus naphtha which finds today several uses. He also referred to the utilisation of slags in which the National Metallurgical Laboratory had made valuable contributions. In concluding, Prof. Kabir

A view of the distinguished delegates at the inaugural session of the Symposium.

congratulated Dr Nijhawan and his colleagues on organising such International Symposia and on the splendid work in diverse fields—he expressed the hope that the annual symposia of the National Metallurgical Laboratory would not only develop international scientific collaboration but would also lead to the consolidation of brotherhood and mutual help between all scientists of the world.

Technical sessions

Thirty-seven technical papers covering research and development work on utilisation of metallurgical wastes were presented and discussed in six technical sessions relating to (i) Treatment of fines, and other low grade by-product materials produced during mining and by mineral beneficiation plants, (ii) Utilisation of by-products and wastes produced in pyro-, hydro-, and other extractive metallurgical, smelting and refining operations, (iii) Utilisation of waste gases and flue dusts produced during roasting, smelting and refining and economics of recovery operations, (iv) Utilisation of metallic scraps, drosses, ashes and skimmings, swarfs and residues resulting from ferrous and non-ferrous metallurgical refining and processing operations, (v) Utilisation of spent pickle liquors and recovery of metallic values from waste solutions, (vi) Theoretical considerations of recovery of by-products and utilisation of metallurgical wastes.

Utilisation of raw material wastes and by-products

The first Technical Session opened with 5 papers on the utilisation of raw material wastes and by-products.

Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, while dwelling on the 'vitally important' subject of utilisation of metallurgical wastes, gave a comprehensive review of the research and development work undertaken at the National Metallurgical Laboratory on diverse phases of the problem and outlined the potential field for further development work. Systematic studies undertaken in the NML, Dr Nijhawan said, had embraced a vast field including both short term and long range research projects on the following basis :

1. Treatment of mining rejects and mineral discards, such as of ore fines and other low grade by-products—their beneficiation, processing and optimum utilisation.
2. Utilisation of slags and residues ; treatment of by-products of metal industries, such as of blast furnace and steel slags, flue dusts, millscale, coke breeze, etc.
3. Utilisation of drosses, swarfs, skimmings, such as of zinc dross from galvanizing shops, aluminium dross, reclamation of lead and processing of electrometallurgical residues and muds.
4. Utilisation of metallurgical waste gases, such as during electric smelting of ferro-manganese and related fields.
5. Miscellaneous utilisation studies, such as of steel scrap reclamation, refractories raw materials, etc.
6. Scientific research studies such as relating to mineralogy and slag phase systems based on hot stage microscopy, X-ray diffraction analyses and other physical methods of examination of metallurgical by-products and wastes.

It is well established today that research and development work in these fields can hardly be considered complete in most of its phases and yet in some cases

Group photograph of some of the delegates to the Symposium.

industrial scale implementation of the research results has been readily forthcoming based on the economic acceptability and metallurgical feasibility of the investigations conducted at the National Metallurgical Laboratory.

The problem of utilisation of ore fines, Dr Nijhawan added, is of topical interest in India. He emphasised that these fields demanded a well planned programme of work to be steadily and systematically executed. Mechanized iron ore mining, crushing and screening released up to 40% of ore fines which are at present dumped as waste and it has been estimated that by the end of the Third Five Year Plan, 11 to 12 million tonnes of ore fines will be dumped, representing a loss of Rs 60 million.

Mr J. Astier of IRSID, France, outlined the industrial development of sinter in his country and presented pilot plant data relating to pelletizing of Lorraine iron ores. In his opinion blast furnaces operated at their best when charged with high sinter burden especially 100% self-fluxing sinter. As far as pelletizing is concerned, he pointed out that it might become necessary in the near future to carefully compare it with sintering before making a final choice of process for agglomerating iron ores.

Messrs M. S. Chopra, G. P. Mathur and P. I. A. Narayanan (NML) gave a broad appraisal of work carried out on Indian iron ore fines and blue dust at the National Metallurgical Laboratory through exhaustive tests which have yielded positive results. The methods of utilisation of these fines after suitable agglomeration by sintering and pelletizing have also been worked out. The authors also referred to the beneficiation work in progress in the laboratory on low grade manganese, chrome, iron ores, non-metallic minerals, etc. from various parts of India and presented the experimental results achieved so far at the Mineral Beneficiation Pilot Plant of NML. The use of beneficiation techniques was strongly recommended for the utilisation of the mining and metallurgical wastes and consequent conservation of these resources wherever physical separation of the valuables is found feasible.

Large quantities of fine grained raw materials are produced during the smelting of ferro-manganese. The National Metallurgical Laboratory has investigated the possibility of utilising such materials for making self-fluxing briquettes suited to electrothermal smelting of ferro-manganese. Dr A. B. Chatterjea and Messrs S. R. Ghosh and J. Goswami (NML), describing the types of binders and various particle sizes that had been tried, stated that while inorganic binders proved to be unsatisfactory, organic binders such as molasses and sulphite lye conferred satisfactory physical properties particularly after heat hardening the briquettes at 200°C. However strength at elevated temperatures was inadequate for smelting purpose but this could be remedied by addition of 5 to 10% coking coal. Briquettes containing 10% coking coal and 4% sulphite lye were found satisfactory for electro-thermal smelting.

Other by-products from the ferro-manganese industry so far considered as wastes are slags carrying away 14 to 16% Mn and furnace gas with 68–70% carbon monoxide, which is discharged into the atmosphere. Messrs C. R. Coil and A. Sangameswara Rao of Ferro Alloys Corporation Ltd., Shreeramnagar, particularly discussed the utilisation of these gases as reducing and heating agents and for the synthesis of methanol and chemicals.

Utilisation of gases in iron and steel production

The gaseous by-products emanating from the iron and steel plants during smelting and refining are rich in carbon monoxide and possess fairly high calorific value which can be safely recovered and utilised for various purposes. In the second Technical Session of the Symposium several papers were presented on the recovery and utilisation of such waste gases in iron- and steelmaking. It was unanimously agreed that unburnt gases can be safely recovered and cleaned and that the utilisation of the latent heat of such waste gases will substantially increase the thermal efficiency of iron and steel processes.

Dr H. Malcor, Chairman, CFAM, France, referred to some difficulties, encountered in collecting the gases issued from steelmaking vessels and described two recovery devices: the tight connection system and the open connection method patented in France. Dr P. A. Young, Director of Research, Head Wrightson, England, then gave an illuminating theoretical analysis of the problem related to LD converters.

It was suggested by Mr J. L. Harrison, of British Oxygen, England, that while the energy can be advantageously utilised to preheat scrap or to reduce fine ores, the fine dust from the furnace cleaning system could be handled in the pre-reducing cycle. A paper from Yawata Iron and Steel Co., Japan, described their experience with the O. G. Process of waste gas recovery. Dr Imai stated the oxygen gas recovery process is quite safe and that the gas recovered contains 70–90% CO. One of their LD vessels was fitted with O.G. equipment and is operating sinch March, 1962.

Messrs B. L. Sen and P. K. Bose of Indian Oxygen, Calcutta, examined the eventuality of low shaft furnaces spread up throughout the country and stated that the economics of such units combined with oxygen steelmaking process cannot be satisfactorily balanced without a very effective use of waste heat and gas including their application in other ancillary industries such as cement, fertilizer and chemicals based on steel plants by-products. Dr S. C. Sircar and Mr Ya. Ya. Mikhin examined the possibility of nickel extraction from copper matte containing small amounts of nickel and Mr D. V. Jackson, of Warren Spring Laboratory, England, presented his studies on chloride roasting and volatilisation for recovery of non-ferrous metals.

Utilisation of by-products and wastes in iron and steel production

The third session discussed seven technical papers on the utilisation of by-products and wastes in iron and steel production, including metallics from steel mill wastes, which formed the subject of a special paper by Dr William T. Hogan.

With the projected development of steel and other industries, steel plants in India will have to be spread throughout the country including areas having only non-coking coals and inferior ores. Dr W. Janke and Mr L. R. Choudhary of Lurgi, West Germany, described the S. L. direct reduction process and showed on the basis of experimental data that such processes would be of great interest for smelting low grade raw materials.

Investigations were conducted at the National Metallurgical Laboratory on making self-fluxing briquettes containing iron ore fines, coke breeze and limestone dust employing bentonite as a binder and smelting of the briquettes in a small blast furnace designed and fabricated at the National Metallurgical Laboratory. Dr A. B. Chatterjea, Messrs J. G. Goswami, S. K. Biswas, Santok Singh and J. S. Padan discussed the smelting performance of the briquettes on the basis of their operational results with the objective of utilising the abundant coke breeze currently surplus at the steel plants. Mr A. N. Whiting of Davy and United Engg., England, pointed out several advantages of the new STORA process for ironmaking in regions possessing high grade ore but deficient in metallurgical coke. Low grade carbonaceous fuels such as coke breeze and certain types of coal can be used in this process and the total fuel consumption is low. Early indications are that for a small scale operation, for example up to 150 000 tons of pig iron a year, the process is cheaper both in capital and operating costs than other ironmaking processes.

Messrs K. C. Choudhuri and P. K. Munshi from Research, Design and Standards Organisation, Chittaranjan, discussed the utilisation of ferrous scrap on the Indian Railways. They stated that about 14·97 lakh tons of ferrous scrap is produced in India every year which in terms of foreign exchange costs Rs 20 crores. While 186 000 tons are exported and 68 000 tons consumed internally there is an unaccounted balance of 12·43 lakh tons consisting of sheet metal scrap, heavy melting scrap turnings and borings or swarf. The authors also referred to their attempts, in collaboration with the National Metallurgical Laboratory, to utilise high speed steel scrap by melting in an electric furnace and forging it for the manufacture of high speed steel tools.

Utilisation of metallurgical slags

The 4th Technical Session of the NML Symposium was entirely devoted to the subject of utilisation of metallurgical slags. Huge quantities of slags are produced in iron and steel plants. A modern 1 000-ton iron blast furnace yields as much as 600 tons of slags daily which is dumped. Utilisation of industrial slags will not only solve the formidable problem of its disposal but will earn profits to the producers. The percentage of slag utilised in India is negligible and the importance of the problem can be judged from the fact that in West Germany not only all the slag produced is utilised but more is collected from their old dumps. The USA also consumes the entire quantity of slag produced.

Messrs Narinder Singh, K. N. Srivastava, R. M. Krishnan and Dr B. R. Nijhawan of NML discussed the scope for utilisation of slags in India and gave a lucid picture of the pattern of consumption of slags in this country on the basis of the work done at the NML in close co-ordination with the Indian steel plants. They stated that industrial slags have a multitude of uses such as in slag cement aggregate for concrete, road making, rail road ballast, slag wool, seewage filter media, filler material, foamed aggregate for light weight thermal and accoustic insulation concrete. The authors presented their experimental results on the production of light weight insulation concrete from slags produced at the Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory. The slag aggregate produced conformed to ASTM specifications and gave very promising results. Another NML paper by Messrs B. N. Singh, P. C. Debnath and Dr B. C. Kar examined the suitability of low shaft furnace slag for the production of slag cement and stated that the cement obtained used with Portland cement as activator conforms to American, British and Indian Standards specifications. Current studies on the utilisation of Rourkela slag, in progress in the Central Building Research Institute, Roorkee, CSIR, were reported by Messrs S. K. Chopra and C. A. Taneja.

Slag wool, which is mainly used for insulation purposes, is manufactured in Jamshedpur from blast furnace slag. Its total demand in India by the end of 1964 is estimated at 12 000 tons per annum. Mr. R. P. Punj, Jamshedpur, described the manufacturing processes and quality control techniques employed in the production of slag wool.

At Tisco, Jamshedpur, 97% of the blast furnace gas is utilised and flue dust has been used in sinter mix. About 300 tonnes of slag are granulated per day for the cement plant at Jhinkpani. Messrs B. P. Singh and Parvez M. Mehta stated that flue dust and sludge which are not utilised at present will be used with sinter mix in the future. Messrs H. Klier and L. R. Choudhary confirmed the possibilities of such uses on the basis of their work at Lurgi, West Germany.

Utilisation of non-ferrous scrap and recovery of by-products

The annual requirements of different non-ferrous virgin metals on Indian Railways and the types of scrap available were reviewed by Mr K. C. Choudhuri and P. K. Munshi—Research, Design and Standards Organisation, Chittaranjan—who outlined the various methods of reclamation particularly the Sigma Oil Method, the Bradley Process and the Differential Melting Process for separation of bronze borings mixed with white metal and reclamation of scrap lead batteries. Large quantities of red mud are currently dumped to waste at aluminium production plants in India. In the background of the researches carried out at the National Metallurgical Laboratory, Messrs C. Sankaran and P. P. Bhatnagar discussed the possibilities of recovering iron, aluminium, titanium and vanadium oxides from the red mud. The results of their investigations on the recovery of alumina values from a red mud sample by soda ash and limestone roasting were also reported and discussed in the background of various operating factors and the possibilities of utilising the residue to produce pig iron and titania rich slag or the ferro-titanium. Messrs M. C. Sen and Dr T. Banerjee (NML) reviewing the production of secondary aluminium stated that though the country has sufficient reserves of bauxite to satisfy the requirements of primary aluminium production, the necessity of secondary aluminium production assumes great importance when considering several factors other than the availability of the ores, such as electricity, for example, which is scarce in our country and high in tariff. Mr K.K. Cherian of Indian Aluminium Co., Alupuram, also dealt with metallurgical wastes from aluminium smelters.

Vanadium is widely used in the production of various alloy steels and its compounds are employed in increasing quantities in different industrial oxidation processes. Dr N. Venkataraman and Dr M. S. Thakar (Indian Aluminium Co. Ltd., Ghotamuri) examined the possibilities of isolating vanadium salts from the Bayer plant liquors where they find their way as an undesirable impurity while processing bauxite for the production of alumina and described a process for recovery of soda from this salt and elimination of a vanadium rich sludge.

With the gradual mechanization of Indian industries more and more battery scrap will be available in the country. A paper from Lurgi, West Germany, described a short rotary furnace well suited for the treatment of battery scrap. Mr K. Roychowdhury, Eyre Smelting, Calcutta, also stressed the importance of recovery of lead and its alloys from scrap in the background of current

Utilisation of pickle liquors and miscellaneous residues

The satisfactory disposal of effluents from the steel plants pickle liquor had plagued the industry for generations. Pickle liquor disposal had been tackled for over fifty years to find a technically and economically satisfactory solution. Apart from recovering usable by-products by the industries, the problem of preventing stream pollution had received great attention from the public health agencies and industry alike. A paper from Lurgi, West Germany, by Mr H. Welling described the Lurgi process of pickle liquor regeneration by vacuum crystallisation while Mr K. Tamaki explained a process developed by Fuji Iron and Steel Company, Japan. Messrs V. Kramarsic, F. Strojin and Prof. Ing. Ciril Rekar from Metallurgical Institute, Yugoslavia, also dealt with a new process for regeneration of ferrous sulphate pickle liquor which yields mineral pigments or magnetite. Dr G. K. Seth and Mr Y. S. Murty, Central Public Health Engg. Research Institute, Hyderabad Zonal Centre, discussed the treatment and recovery of by-products from pickling liquor wastes and detailed the economics of neutralisation with lime and recovery of ferrous sulphate and sulphuric acid under Indian conditions.

The recovery of zinc from scrap and wastes was discussed at length by Messrs B. C. Mukherjee, S. C. Aush, M. C. Sen and Dr T. Banerjee on the basis of the results of studies made at the National Metallurgical Laboratory for the recovery of zinc and zinc oxide from a sample of treated zinc ash. Utilisation of galvaniser's dross was stressed in a paper by Dr M. N. Parthasarathy and B. C. Agarwal, Indian Lead/Zinc Information Centre, who reviewed the well known processes of recovery of zinc and their economics.

In a resume of the Symposium at the end of the technical sessions Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, observed that the papers submitted covered multitudinous aspects of utilisation of metallurgical wastes which represent a vast and challenging field. The seriousness of some of the problems encountered was reflected by the practical steps and measures suggested in most of the papers which stimulated very lively and constructive discussions of immense practical value. Viewed in the context of national economy and self-sufficiency, the NML Symposium on 'Utilisation of Metallurgical Wastes' was most opportune in focussing the attention of India's industrialists—both in the public and private sectors—government authorities and research workers both at home and abroad on the importance and urgency of expanding and consolidating work in this vast field. The international character borne by the Symposium is convincing proof that it did succeed in rousing the interests of all concerned and thus fulfilled the very objective for which it was held. The Symposium concluded with conducted visits round the National Metallurgical Laboratory and its pilot plants, including the Low Shaft Furnace and the Mineral Beneficiation Pilot Plant.

Growth Pattern of Iron and Steel Industry in India's Economic Development

B. R. Nijhawan

The current annual production of finished steel is just over 4 million tonnes in India. The growth pattern of Indian iron and steel industry from current production figures to a production capacity of over 20 million tonnes of crude steel at the end of the Fourth Five Year Plan, has been outlined stage by stage and rationally analysed. The individual expansion pattern of different steel plants currently operating in India has also been outlined in relation to estimated requirements of finished steel by 1970–71.

Likewise, the growth pattern of foundry pig iron from the current produciton of just over a million tonnes a year to over 4 million tonnes annual capacity to be established by the end of the Fourth Five Year Plan, has been outlined whilst highlighting current shortfalls of foundry pig iron in the country.

The establishment and projected growth of alloy, tool, special and stainless steel industry in India have likewise been analysed in relation to its growth pattern to be followed till the end of the Fourth Five Year Plan. The estimated short-term and long-range requirements of the diverse ranges of ferro-alloys to cater to the needs of the alloy, tool, special and stainless steel industry have been outlined in relation to Third and Fourth Five Year Plans including the financial implications of the ferro-alloys' requirements.

The role of Indian raw materials such as iron ore and flux, their inherent shortcomings and optimum remedial beneficiation treatments required have been discussed in relation to their indispensability in satisfying the growth pattern of Indian iron and steel industry. The role of small foundry iron production plants has been specifically highlighted in relation to integrated iron and steel complexes in the background of Indian conditions and projected developments.

It has been shown that even though the iron and steel industry is highly capital intensive, it cannot be left to the vagaries of international trade both in times of peace and that of war to satisfy the almost unlimited applications of iron and steel product-mix in light, medium and heavy engineering and consumer industries. The paper outlines the current planning of Indian iron and steel industry and its steady growth during the successive Five Year Plans to assist the country to attain the economic 'take-off' stage. Of necessity, such an upward growth of the basic heavy steel industry entails its inevitable toil and sweat, success and pitfalls and yet the ultimate objective of attaining Indian self-sufficiency in iron and steel industry is undisputed, provided, however, metallurgical problems of the raw materials, installation and maintenance of iron and steel plants at their peak operational efficiency are squarely faced and effectively overcome and not lost sight of in the maze of endless discussions and explanations.

THE hard core of long-term planning in India as embodied in our successive Five Year Plans has been the establishment of 'heavy' industry in its diverse phases including the growth of integrated iron and steel complexes and a network of small plants based on resources of men and materials essentially indigenous. Whilst the capital outlay for the establishment of pillars of heavy industry and tandem growth of medium and light industries have followed certain characteristic pattern influenced by constraints imposed by our balance of payments and thereby based on friendly aid wherever possible, the reliance on capital fundamentally indigenous has been basic.

The main objectives of economic planning in India are to raise the standards of living of India's multitude, provision of adequate opportunities for the development of indigenous talent and economic industrial growth in the ultimate analyses on "one's own legs". These short-term and long-range purposeful, sustained and titanic economic planning and growth have not been without the inevitable toil and sweat and problems arising in the maze of rapidly expanding horizons of research and technology, of technical education and mass literacy and deepening challenges of war against poverty within and a foe beyond. Such then is the broad-based spectrum of the ancient and modern India ; the ancient still standing true and majestic and the modern shimmering into industrial nationhood.

Modern technology and steel production

The impact of modern technological developments in the metallurgy of iron and steel production, has been square and ever-lasting on Indian iron and steel industry. The metallurgy of iron and steel is based on processes that have essentially remained unaltered in essence over the past century but have undergone spectacular changes in the scale of operations and efficient processing of raw materials and 'refining' techniques based essentially on contemporary developments in engineering technology. It is now well established that iron and steel are basic to heavy industrialisation in any country. The problems that confront India are complex relating chiefly to difficulties of foreign exchange, raising of productivity potential, shortage of technical trained personnel and insular shortages of indigenous capital goods and maintenance spares. In spite of vast good grade iron ore proved reserves of over 20 000 million tonnes, the heavy expansion of steel industry has revealed some basic deficiencies in the raw materials ; high alumina contents and unfavourable Al_2O_3/SiO_2 ratio of Indian iron ores particularly in the ore fines aggravated by heavy monsoon rains, high ash contents of Indian metallurgical coals, shortage of steelmaking quality limestone flux, etc. are characteristic of the situation. The reserves of metallurgical coal are not only limited but also concentrated in eastern India and generally have high ash contents that make their expensive washing 'a must'. The basic steelmaking flux i.e. Indian limestones are exceedingly high in

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Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, Jamshedpur. The paper was presented at the Unesco Inter-Regional Symposium on 'The Application of Modern Technical Practices in the Iron and Steel Industry to Developing Countries' held at Prague, Czechoslovakia, in November 1963.

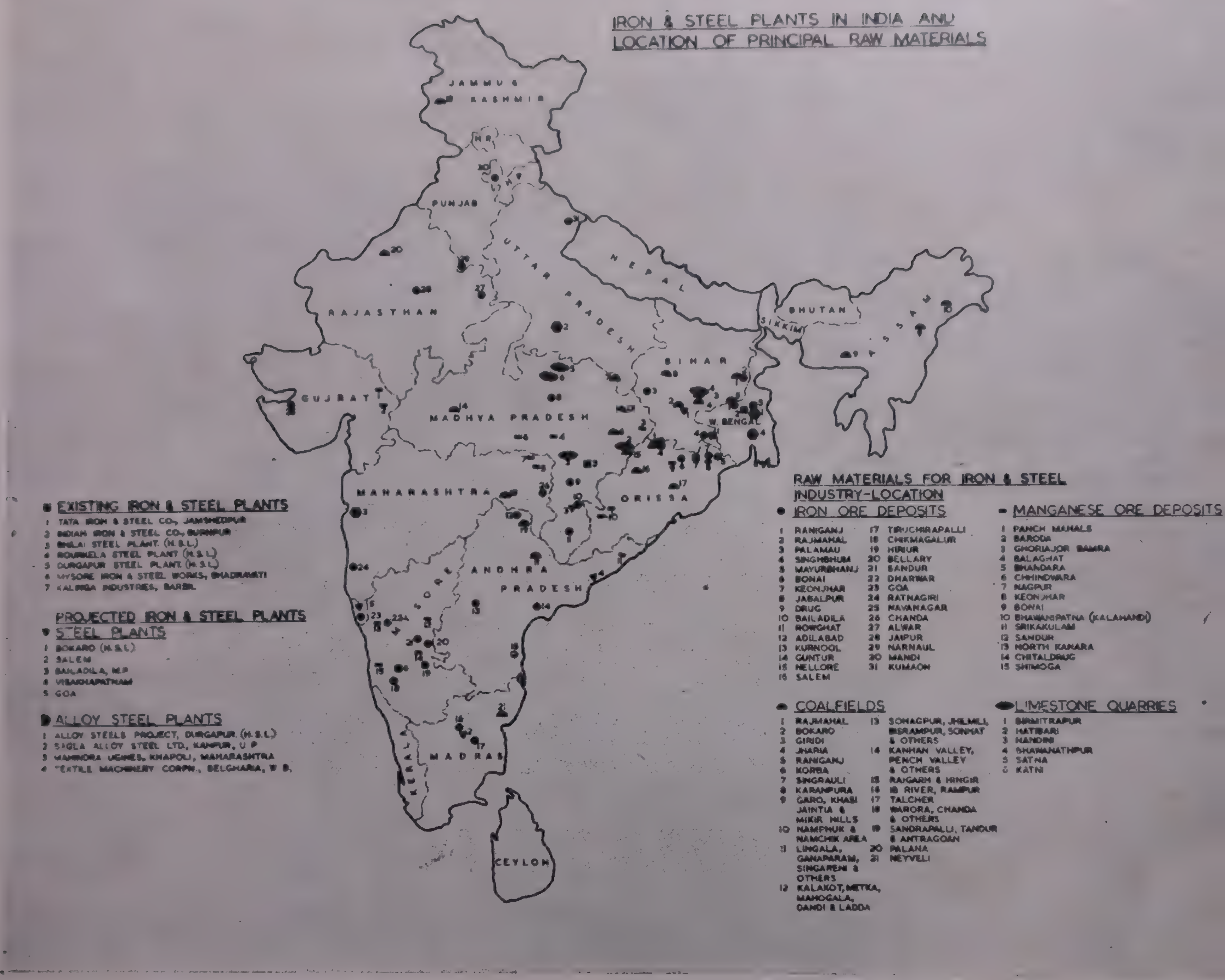
insolubles', tending to change the 'steelmaking' into 'slag-making', from a metallurgical 'metaphor' to an undesirable reality. The conjoint ill effects of such problems are obvious considered in the context that India's annual ingot steel production capacity which is now being expanded from 6 million to about 9–10 million tonnes at the end of Third Five Year Plan (1965–66), is further projected to yield at the end of the Fourth Five Year Plan (1970–71) an annual production of 18 million tonnes of ingot steel necessitating the establishment of a steelmaking capacity of 20-21 million tonnes a year, thereby yielding 13·6-14 million tonnes of finished and rolled steel products. These developments have been planned on the basis that at no time during the Third and Fourth Five Year Plans is there any possibility of supplies exceeding demands, despite the current emphasis on exports. A demand of 6·9–7 million tonnes per year of rolled and finished steel products at the end of Third Five Year Plan (1965-66) has been established corresponding to over 9 million tonnes of annual ingot steel production to be achieved on the basis of the following break-up :

Existing steel plants	Million tonnes per year (ingot steel)
Tata Iron and Steel Works	2
Indian Iron and Steel Works	1
Bhilai (Hindustan Steel Ltd) (after current expansion in hand)	2·5
Rourkela (Hindustan Steel Ltd) (after current expansion in hand)	1·8
Durgapur (Hindustan Steel Ltd) (after current expansion in hand)	1·6
Miscellaneous small units	0·1
	9·0

The maximum actual output from the existing plants and their current expansion plans under execution may yield 6·86-6·9 million tonnes per year of finished steel equivalent to over 9 million tonnes of ingot steel, provided the attainment of almost 100% production of the rated capacity, is physically achieved at the end of the Third Five Year Plan, which however in actual practice could be problematical. In these schemes, a million tonnes per year of ingot steel output from the projected Bokaro Steel Plant at the end of the Third Five Year Plan had to be excluded ; the Third Five Year Plan had originally been planned to yield an ingot steel production of over 10 million tonnes per year during 1965–66 subject, of course, to actual steel production and installed capacity fully matching each other. These plans have now been supplemented by additional targets of about 6·75 million tonnes of rolled and finished steel to be accounted for at the end of the Fourth Five Year Plan (1970-71) corresponding to 8·8 million tonnes annually of ingot steel and adding up to a total of about 18 million tonnes of ingot steel per year, or about 13·6–14 million tonnes annually of finished rolled steel. These plans, formidable under Indian conditions of scanty capital goods, trained men and materials, yet dynamic judged by any yardstick, have to be fulfilled through expansion by the end of the Fourth Five Year Plan (1970-71) of production capacities on the following basis :

Steel plants	Million tonnes/year ingot steel
Bhilai (Hindustan Steel Ltd)	3·25
Durgapur (Hindustan Steel Ltd)	3·0
Rourkela (Hindustan Steel Ltd)	2·5
Tata Iron and Steel Works	3·0
Indian Iron and Steel Works	2·0
	13·75 m. tonnes capacity of ingot steel

from the above plants during 1970–71 may however be somewhat less than 13·75 million tonnes. To the above total may be added 3 million tonnes a year of ingot steel production from the projected Bokaro Steel Plant decidedly to be established on the basis that an annual capacity of 4 to 4·5 million tonnes of ingot steel production for Bokaro Steel Plant would possibly have been created by 1970–71. Additionally the South Indian Iron and Steel Plant based on the use of Salem magnetite and Neyveli lignite may be expected to yield 0·5 million tonnes of ingot steel annually during the Fourth Five Year Plan. Even apart from the South Indian Steel Plant, an annual ingot steel production of 16·75 m. tonnes has thus been planned. To meet, however, the projected figure of 18 million tonnes a year of ingot steel production by 1970–71, additional steel capacity would need to be set up, specifically more so since to physically attain 18 million tonnes of ingot steel annual production, a production capacity fairly in excess thereof would be necessary on the premise that actual steel production and the rated capacity will not always and at least during the initial 'teething' periods fully match each other. To meet these requirements, two additional steel plants at new locations currently under study would be established, each with an annual ingot steel capacity of 1·5 million tonnes ; this would give an annual total of 19·75 or say about 20 million tonnes of crude steel production capacity projected by 1970–71. In this connection, the Hindustan Steel have started a survey of the Bailadilla (Madhya Pradesh)-Vishakapatnam belt whilst Government of India's noted steel consultants, Messrs Dastur and Company, are likewise actively surveying the Bellari (Andhra Pradesh)-Hospet (Mysore) belt and Goa coastal area for future steel plants to be set up during the Fourth Five Year Plan. These steel plants, though designed for an initial annual production of 1·5 million tonnes of ingot steel by the end of the Fourth Five Year Plan, would also be capable of expansion to an annual capacity in each case of 3–4 million tonnes of crude steel. The establishment and growth of coastal plants, such as at Goa, may also favourably consider the import of high grade metallurgical coking coal or coke to be balanced against the export of iron ore pellets made out of beneficiated iron ore fines from Goa mines at a price of about 12 dollars a tonne. It is a welcome feature of current Indian planning that the establishment of new steel plants is distinctly more 'raw materials' oriented' rather than solely 'equipment-oriented'. Among the items to be produced in these steel plants, the flat products would predominate since the deficit is particularly noticeable in diverse flat products. The magnitude of planning and scale of operations, it would be appreciated, are truly titanic, more so when the production has to be systematically rationalised and oriented to optimum end-product mix based on advance yet comprehensive market surveys. Current thinking also favours the building up of stocks of say 1–1·5 million tonnes of steel by 1970–71 to withstand the strains of war and stresses of peace ; such planning is in conformity with the rationale of India's accelerated steel development plans so that India can not only hope eventually to become the 'Workshop of the East' linking her exports of a multitude of end-products with assured physical supplies of home-made steel but would also attempt to regain the position she once had as the cheapest steel producer in the world.

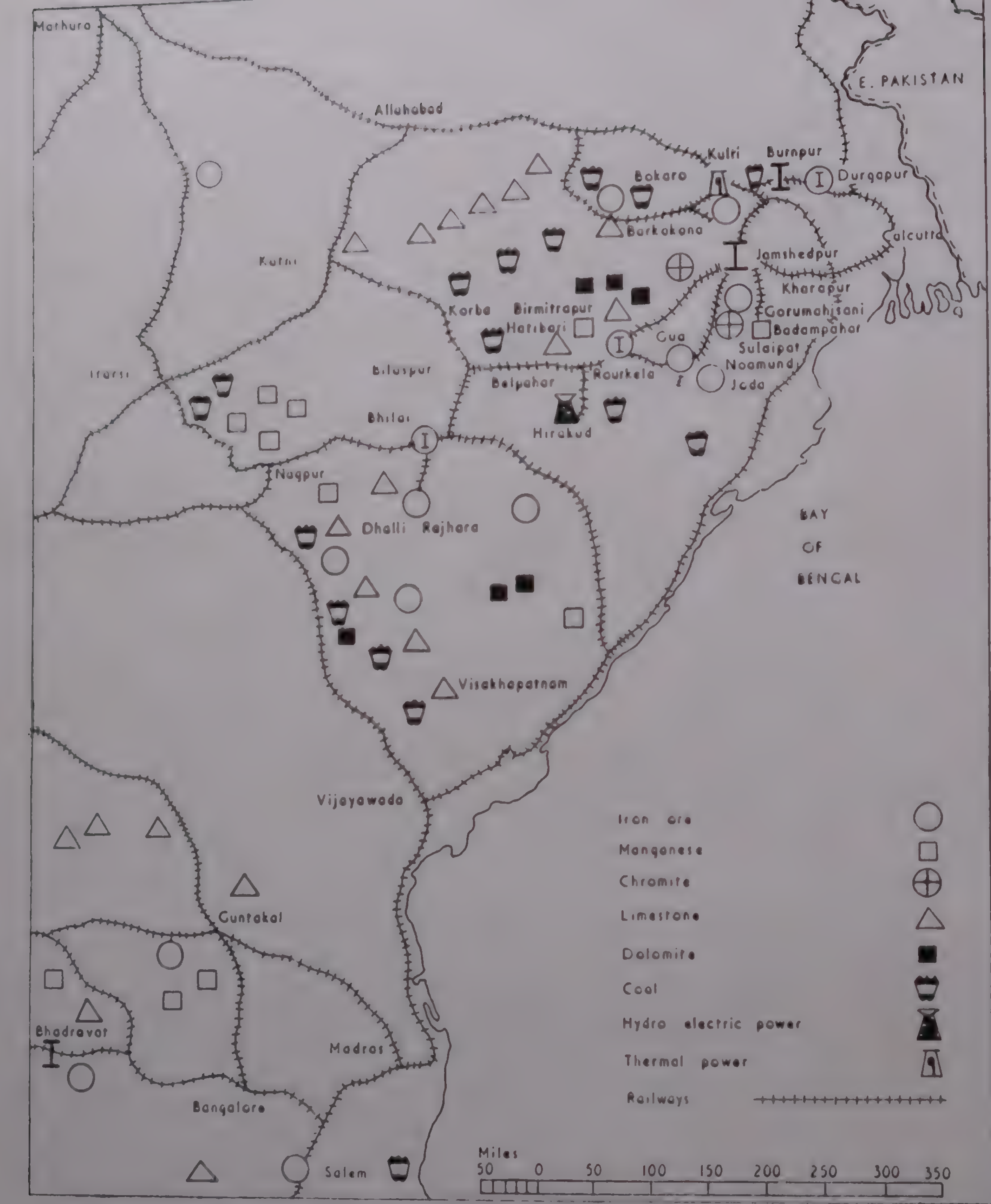

IRON & STEEL PLANTS IN INDIA AND LOCATION OF PRINCIPAL RAW MATERIALS
JAMMU & KASHMIR
H.P.
PUNJAB
RAJASTHAN
UTTAR PRADESH
NEPAL
BHUTAN
SIKKIM
ASSAM
BIHAR
W. BENGAL
GUJRAT
MADHYA PRADESH
MAHARASHTRA
ORISSA
MYSORE
ANDHRA PRADESH
KERALA
MADRAS
CEYLON
EXISTING IRON & STEEL PLANTS
1 TATA IRON & STEEL CO., JAMSHEDPUR
2 INDIAN IRON & STEEL CO., BURNPUR
3 BHILAI STEEL PLANT. (H.S.L.)
4 ROURKELA STEEL PLANT (H.S.L.)
5 DURGAPUR STEEL PLANT (H.S.L.)
6 MYSORE IRON & STEEL WORKS, BHADRAVATI
7 KALINGA INDUSTRIES, BARBIL
PROJECTED IRON & STEEL PLANTS
STEEL PLANTS
1 BOKARO (H.S.L.)
2 SALEM
3 BAILADILA, M.P
4 VISAKHAPATNAM
5 GOA
ALLOY STEEL PLANTS
1 ALLOY STEELS PROJECT, DURGAPUR. (H.S.L.)
2 SAGLA ALLOY STEEL LTD., KANPUR, U P
3 MAHINDRA UGINES, KHAPOLI, MAHARASHTRA
4 TEXTILE MACHINERY CORPN., BELGHARIA, W B.
RAW MATERIALS FOR IRON & STEEL INDUSTRY-LOCATION
IRON ORE DEPOSITS
1 RANIGANJ
2 RAJMAHAL
3 PALAMAU
4 SINGHBHUM
5 MAYURBHANJ
6 BONAI
7 KEONJHAR
8 JABALPUR
9 DRUG
10 BAILADILA
11 ROWGHAT
12 ADILABAD
13 KURNOOL
14 GUNTUR
15 NELLORE
16 SALEM
17 TIRUCHIRAPALLI
18 CHIKMAGALUR
19 HIRIUR
20 BELLARY
21 SANDUR
22 DHARWAR
23 GOA
24 RATNAGIRI
25 NAVANAGAR
26 CHANDA
27 ALWAR
28 JAIPUR
29 NARNAUL
30 MANDI
31 KUMAON
MANGANESE ORE DEPOSITS
1 PANCH MAHALS
2 BARODA
3 GHORIAJOR BAMRA
4 BALAGHAT
5 BHANDARA
6 CHHINDWARA
7 NAGPUR
8 KEONJHAR
9 BONAI
10 BHAWANIPATNA (KALAHANDI)
11 SRIKAKULAM
12 SANDUR
13 NORTH KANARA
14 CHITALDRUG
15 SHIMOGA
COALFIELDS
1 RAJMAHAL
2 BOKARO
3 GIRIDI
4 JHARIA
5 RANIGANJ
6 KORBA
7 SINGRAULI
8 KARANPURA
9 GARO, KHASI JAINTIA & MIKIR HILLS
10 NAMPHUK & NAMCHIK AREA
11 LINGALA, GANAPARAM, SINGARENI & OTHERS
12 KALAKOT, METKA, MAHOGALA, DANDI & LADDA
13 SOHAGPUR, JHILMILI, BISRAMPUR, SONHAT & OTHERS
14 KANHAN VALLEY, PENCH VALLEY & OTHERS
15 RAIGARH & HINGIR
16 IB RIVER, RAMPUR
17 TALCHER
18 WARORA, CHANDA & OTHERS
19 SANDRAPALLI, TANDUR & ANTRAGOAN
20 PALANA
21 NEYVELI
LIMESTONE QUARRIES
1 BIRMITRAPUR
2 HATIBARI
3 NANDINI
4 BHAWANATHPUR
5 SATNA
6 KATNI

1 *Iron and steel plants in India and location of principal raw materials.*

Ambitious planning and the problems

Before, however, these plans can physically mature, complicated and difficult problems will have to be tackled, such as breaking new grounds in respect of raw materials' bases and their speedy development following the new well-established criterion that the raw materials will need optimum processing and sizing and possibly additional economic beneficiation treatments. The physical transport of raw materials by rail is one of the most formidable problems which can seriously stand in the way of economic planning particularly in attaining steel production targets. The shortage of technically trained man-power, skilled artisans and competent supervisory managerial personnel completes the picture, particularly when it is realised that the period of useful technical training can only be abridged marginally considered on the basis of its ultimate utility. These then are some of India's steel hopes and ambitions, physical difficulties and chronic shortages, which, however unsurmountable at first sight, would need to be and are being effectively met and overcome as challenges to Indian ingenuity and skill. The serious intensity of the entire forward planning and current problems would be judged from the position that production of finished steel during 196–263 was 3·9 million tonnes, 100 000 tonnes less than the target. The 4·3 million tonnes target for 1963–64 may, however, be achieved whilst production targets for subsequent years would suffer due to the delay in putting up the Bokaro Steel Plant—for instance, the target of 6·8 m. tonnes of finished steel for 1965–66 would be reduced by 900 000 tonnes owing to delay in putting up the projected Bokaro Steel Plant.

In the ultimate analysis, there may also be some adjustments necessary such as possible doubling of Durgapur Steel Plant's annual capacity from 1·6 million tonnes of crude steel to 3·2 million tonnes by the end of the Fourth Five Year Plan. It is also planned that Bokaro Steel Plant will be initially designed for an ultimate annual production capacity of 4 to 4·5 million tonnes and may attain an operational capacity of 3 million tonnes per year by the end of the Fourth Five Year Plan—to this could be added at least 1·5 million tonnes/year


Mathura
Allahabad
E. PAKISTAN
Kulti
Burnpur
Durgapur
Bokaro
Barkakana
Calcutta
Jamshedpur
Kharapur
Gorumahisani
Badampahar
Sulaipat
Noamundi
Joda
Gua
Katni
Korba
Birmitrapur
Hatibari
Itarsi
Bilaspur
Belpahar
Rourkela
Hirakud
Bhilai
Nagpur
Dhalli Rajhara
BAY OF BENGAL
Visakhapatnam
Vijayawada
Guntakal
Bhadravat
Madras
Bangalore
Salem
Iron ore
Manganese
Chromite
Limestone
Dolomite
Coal
Hydro electric power
Thermal power
Railways
Miles
50 0 50 100 150 200 250 300 350

2 *Resources of raw materials for iron and steel plants.*

from each of two proposed steel plants to be set up during the Fourth Five Year Plan, whilst the maximum planned capacity of these two new steel plants, other than the Bokaro Plant, would be 4 million tonnes per year of crude steel in each case.

Whilst the foregoing reviews the planning data, the role of reserach and development themes in Indian steel industry including long-range study of Indian raw materials for their exploitation by techniques conventional or hitherto unknown, imposes additional yet welcome responsibilities on indigenous research talent—these aspects of advance planning are being effectively handled at the National Metallurgical Laboratory in the fields of raw materials' beneficiation and processing, burden preparations based on sizing, classification, agglomeration and sintering, etc. in relation to conventional and alternative iron and steel production techniques that are today the symbols of increased productivity and lowered operational and production costs.

Figures 1 and 2 show the map of India indicating the principal iron and steel production centres and resources of raw materials including projected steel plants as also the projected alloy steel plants, etc.

It would be only right to realistically introduce an urgent element of 'realism' in the execution of our long-range and short-term steel plants based on the closest possible co-ordination and urgent sense of responsibility at all levels of Projects' planning and their implementation; it is, however, not always so easy in fast developing countries, such as India wherein the multiple planned demands of a free human society are enormous indeed in their scope and still more so in their effective implementation. And yet the challenge must be met clear and square by the free Indian society.

Foundry pig iron

The current annual availability of foundry grades of pig iron is estimated at 1·1 million tonnes whilst the approximate present demand as estimated by trade bodies is of the order of 2·5 million tonnes per year—an earlier estimate of 2·0 million tonnes of foundry pig iron per year is based on 1·1 million tonnes for centrally listed foundries and 0·9 million tonnes for State list foundries. The available 1·1 million tonnes a year foundry pig iron is distributed in the following order: steel works maintenance 100 000 tonnes, railway sleepers 300 000 tonnes, spun pipe 187 000 tonnes, direct ordnance demands 60 000 tonnes, export promotion 50 000 tonnes, castings needed by Directorate-General, Supplies and Disposals 30 000 tonnes, railway maintenance and other government departments 50 000 tonnes, foundries engaged on ordnance contracts 20 000 tonnes, Central list foundries 176 000 tonnes and State listed foundries 120 000 tonnes and reserve stock 7 000 tonnes.

Estimates and planning

Whilst estimates made by different Indian industrial and trade bodies for total current requirements of foundry grades of pig iron and those projected at the end of the Third and Fourth Five Year Plans somewhat differ, it has been generally accepted that by the end of the Third Five Year Plan, the demand would be over 2·006 million tonnes per year and 3·462 to 4 million tonnes per year by the end of the Fourth Five Year Plan whilst the annual established capacity of foundry grade pig iron at the end of the Third Five Year Plan may not exceed 1·5–1·75 million tonnes thereby making it imperative to raise an additional capacity of over 2 million tonnes per year of foundry iron chiefly during the Fourth Five Year Plan. The production capacity expected by the end of the Third Five Year Plan would be based on supplies from the existing plants and the small foundry iron plants for which several industrial licences have already been granted to account for 0·6–0·8 million tonnes annual output, if all the licences are actually operated during the period; this would, however, mean that an additional annual capacity of 2 million tonnes of foundry grades of iron would need to be established by the end of the Fourth Five Year Plan. The heavy shortfalls in foundry iron production figures today and during consecutive Plan periods provide enough food for thought and action and a challenge indeed to be met. Whilst it may be that this shortfall has been inherited from one Plan to another it is, however, most necessary for us to break away from this 'heritage'. The estimate of 3·5 million tonnes of foundry iron made by the National Council of Applied Economic Research for the end of the Fourth Five Year Plan is however now recognized as low and plans are underway to establish a capacity of 4 million tonnes of foundry iron annual output by 1970–71. The National Council of Applied Economic Research estimates are based on the following: *

	Estimated requirements, tonnes	
	1965–66	1970–71
Pig iron for iron castings including steel pipe fittings	1 377 000	2 232 900
Pig iron for cast iron pipes and specials	628 900	1 229 000
Total	2 005 900	3 461 900

Current production figures for saleable pig iron during 1961 and 1962 are given in Table I.†

TABLE I Production figures of saleable pig iron

Plant	1961	1962
Tata Iron and Steel Co.	20 868	21 112
Indian Iron and Steel Co.	267 873	204 298
Mysore Iron and Steel Works	9 934	...
Rourkela (HSL) Plant	99 370	60 246
Bhilai (HSL) Plant	393 442	334 390
Durgapur (HSL) Plant	314 792	325 016
Kalinga Works (Barbil)	30 255	28 469
Total	1 136 534	973 531

Alloy, tool, special and stainless steels

Estimates for the requirements of alloy, tool, special and stainless steels have received due attention from Indian planners for establishment of requisite production capacity. The author had made some estimates way back in 1955-56 at the International Symposium organised by the National Metallurgical Laboratory on 'Production, Properties and Applications of Alloy and Special Steels' that the minimum requirements of the special alloy steels in relation to 10 million tonnes of mild and plain carbon rolled and structural steels per year would be at the very minimum 0·5 million tonnes which were adjudged distinctly to be on the lower side. It has been argued that if India were to take her rightful place in the comity of nations as a modern powerful and heavily industrialized Republic, as justified by her mineral potential and resources, it was appropriate to err on the higher side of the estimates. It should not be overlooked that India can be potential exporter of alloy and special steels to South Eastern countries, East Asian and Far Eastern countries, where such specialized products should prove valuable bargaining counters for the import of material resources in which India is so short. As such, a target of a million tonnes of alloy, tool, special and stainless steels at the start of the Fourth Five Year Plan should be set. Since at the end of the Fourth Five Year Plan, a production target of 18–20 million tonnes of non-alloy steel is to be attained, the corresponding annual target for alloy, tool, special and stainless steels would be 1·8 to 2 million tonnes and even this may prove to be somewhat on the lower side for the highly industrialized requirements of the era to come.

Table II gives a break-up of the alloy, tool, special and stainless steels estimates which form the basis of current planning till the end of the Fourth Five Year Plan.

TABLE II Break-up figures for alloy, tool, special and stainless steels till end of Fourth Five Year Plan

	Finished tonnages per year (tonnes)
(a) Alloy constructional steel	250 000
(b) Stainless and heat resisting steels ...	80 000
(c) Electrical steel sheets	180 000
(d) High speed steel, tool steel and die steel	86 000
(e) Spring steel	134 000
(f) Free cutting steel	200 000
(g) Low alloy high strength steels ...	200 000
	1 130 000 tonnes

or say 1 130 000 tonnes corresponding to annual ingot production of 1·89 million tonnes.

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* Reappraisal of Steel Demand, Vol. 1, 1963, National Council of Applied Economic Research, New Delhi.

† Annual Report of the Ministry of Steel and Heavy Industries, 1962–63, Department of Iron and Steel.

At the same time, however, it has rightly been put forth that the production of low alloy high strength steels should be planned on integrated steelworks and not classified as special steels for the purpose of the above estimates. On that basis, the estimates of alloy, tool, special and stainless steels to be established by the end of the Fourth Five Year Plan would be 930 000 tonnes of annual finished alloy steel output, equivalent to 1·55 million tonnes of ingot alloy steel output per year.

At the Durgapur Alloy Steel Plant of the Hindustan Steel Limited (Government of India), in the initial phase, 14 500 tonnes of tool steel, 25 000 tonnes of constructional steel ; 18 000 tonnes of stainless steel and heat resisting steel and 2 500 tonnes of other alloy steels—giving a total of 60 000 tonnes of finished steel, corresponding to a total of 100 000 tonnes of ingot alloy steels—would be produced annually. Durgapur Alloy Steel Plant would ultimately be expanded to 300 000 tonnes per year when the product-mix would be 25 000 tonnes of tool steel, 75 000 tonnes of constructional steels, 60 000 tonnes of stainless steels mainly in sheet form and 20 000 tonnes of other special steels, giving an annual total of 180 000 tonnes of finished alloy steel production. The production of substitute alloy, tool and stainless steels based on indigenous alloying elements will also be taken up at some of the alloy steel plants, such as of the nickel-free austenitic stainless steels developed at the National Metallurgical Laboratory and other substitute compositions like 202-stainless series, etc. Likewise, research and development themes on substitute tool steels, creep resistant alloys, etc. are actively being pursued at the National Metallurgical Laboratory for industrial scale implementation in due course.

Mysore Iron and Steel Works at Bhadravati currently under conversion to an Alloy Steel Plant would annually produce about 70 000 tonnes of finished alloy constructional steels. Total tonnage of alloy steels for which industrial licences have been granted by the Government of India amounts to about 0·48 million tonnes output a year at present.

Ferro-alloys

Estimates of demands of ferro-alloys have been drawn up on the basis of requirements for plain carbon, mild and structural steels and separately for alloy, tool, special and stainless steels ; so far as the requirements for the former are concerned, these would relate chiefly to ferro-manganese and ferro-silicon as follows :

Period	Annual ingot steel output	Ferro-silicon tonnages needed annually	Ferro-manganese needed annually
	(tonnes)	(tonnes)	(tonnes)
End of Third Five Year Plan	10 million	25 000	125 000
End of Fourth Five Year Plan	18 million	45 000	225 000

Likewise, the estimated requirements of ferro-alloys for non-alloy iron and foundry requirements are given in the next column.

ments

Ferro-manganese and ferro-silicon	
At the end of the Third Five Year Plan	Non-alloy iron castings including malleable grade 2 m/tonnes/yr and plain carbon steel castings 110 000 tonnes per year
Ferro-manganese	2 500 tonnes per year
Ferro-silicon	1 500 tonnes per year
At the end of the Fourth Five Year Plan	Iron castings including malleable grade—4 million tonnes/yr and steel castings 300 000 tonnes/yr.
Ferro-manganese	5 200 tonnes per year
Ferro-silicon	3 500 tonnes per year
Requirements of ferro-chrome for non-alloy iron and plain carbon steel foundry requirements :	
At the end of the Third Five Year Plan	950 tonnes/year
At the end of the Fourth Five Year Plan	2 000 tonnes/year

The above figures will include some quantities of ferro-alloys needed for indigenous production of exothermic compounds used in iron and steel foundries.

Consumption of other ferro-alloys for non-alloy iron and plain carbon steel foundries, such as of ferro-molybdenum, ferro-titanium, etc. would be at best marginal in character and is omitted from these estimates. For ferro-phosphorus, however, some provision could be made for the above application viz., 300 tonnes and 500 tonnes by the end of the Third and Fourth Five Year Plans respectively.

The importance of the establishment of ferro-alloy industry to feed the alloy, tool, special and stainless steel industry hardly needs to be emphasised when it is realised that to meet the annual requirements of 0·5 million tonnes a year of alloy, tool, special and stainless steels, the corresponding ferro-alloys requirements would be of the order of 120 000 to 125 000 tonnes per year, including special types of ferro-manganese but excluding all general purposes ferro-manganese and ferro-silicon needed for the production of plain carbon, mild and structural steels.

It would, therefore, be appreciated that unless a ferro-alloy industry is now established, the requisite ferro-alloys will have to be imported entailing tremendous foreign exchange expenditure ; the estimated amount could well exceed Rs 700 million a year to import the ferro-alloys' requiremeuts for a 0·5 million tonnes a year output of alloy steels to be provided for by the end of the Third and at the start of the Fourth Five Year Plan. It is felt that a ferro-alloy plant capable of producing 25 000 tonnes of different grades of ferro-alloys per year should be immediately set up and it should be increased in stepped up phases up to a capacity of 110 000 to 125 000 tonnes per year when the alloy steels' annual production would be expected to be of the order of 500 000 tonnes.

Excepting nickel, molybdenum and cobalt, resources of which hardly exist in India, all other ferro-alloys can be produced from indigenous resources on an industrial scale, provided requisite technical 'know-how' suited to indigengous raw materials is readily developed—in this task of formulating indigenous technical 'know-kow' consistent with acceptable economics of production and requirements of quality output, the National Metallurgical Laboratory is now actively engaged both in laboratory as also pilot plant scale research investigations. With this basic objective of developing indigenous 'know-how' for the production of diverse ranges of ferro-alloys and for formulating electric smelting technique for the indigenous ores, a Pilot Electric Submerged Arc Ferro-alloy Furnace was commissioned at the National Metallurgical Laboratory with a capacity of 1–2 tonnes of different types of ferro-alloys output per day.

The author had earlier furnished some estimates of the ferro-alloy requirements for alloy, tool, special and stainless steel industry at the International Symposium organised by the National Metallurgical Laboratory in February 1962,[1] excluding the requirements for plain carbon, mild and structural tonnage steels which are given in Tables III and IV.

TABLE III **Estimate of ferro-alloy requirements in India for alloy steel industry.**

Ferro-alloys	Alloy, tool, special and stainless steels capacity 200 000 tonnes per year	Alloy, tool, special and stainless steels capacity 375 000 tonnes a year
	(tonnes/year approx.)	
Ferro-chrome (65% Cr)	26 000	50 000
Ferro-silicon (50% Si)	[illegible] 000	15 000
Ferro-manganese (special grades-75% Mn)	3 000	6 000
Electrolytic manganese (99% Mn)	3 500	6 000
Ferro-tungsten (70% W)	2 500	5 000
Ferro-molybdenum (70% Mo)	450	950
Ferro-vanadium (50% V)	300	650
Others	500	1 000
Total	43 240	84 600

TABLE IV **Estimated requirements of carbon-free ferro-alloys and some other ferro-alloys for an annual output of 375 000 tonnes of alloy steel per year.**

Carbon-free ferro-chrome	1 000 tonnes
Ferro-titanium	200 tonnes
Ferro-boron	50 tonnes
Ferro-zirconium	Less than 50 tonnes
Chromium metal (95%)	100 tonnes
Manganese metal (95%)	100 tonnes
Ferro-chrome manganese	Regular demand of nitrogen bearing ferro-chrome and nitrided manganese alloy will be established after the production of nickle-free austenitic stainless steel has been initiated in the country on the basis of researches undertaken at the National Metallurgical Laboratory.
Ferro-molybdenum	950 tonnes

It would thus be seen that a clear scope exists for the production of carbon-free special ferro-alloys by aluminothermic reaction, to meet the requirements of the alloy steel industry. The demand will gradually increase to 10 000 tonnes a year more when the annual production of alloy and special steels rises to 0·5 million tonnes.

The estimated requirements of different types of ferro-alloys including carbon-free ferro-alloys as stated above are given in the Table V for respective estimated output of alloy, tool, special and stainless steels excluding the plain carbon, mild and structural steels.

TABLE V **Estimated requirements of different types of ferro-alloys for respective output of alloy, tool, special and stainless steels**

Ferro-alloys	Alloy, tool, special and stainless steels capacity 500 000 tonnes per year equivalent to present licensed capacity (tonnes)	Alloy, tool, special and stainless steels capacity 1 million tonnes per year at the end of the Third and start of the Fourth Five Year Plan (tonnes)	Alloy, tool, special and stainless steels capacity 1·8–2 million tonnes per year at the end of the Fourth Five Year Plan (tonnes)
Ferro-chrome (65% Cr)	70 000	14 000	260 000
Ferro-silicon (50% Si)	25 000	50 000	95 000
Ferro-manganese (special grades-75% Mn)	10 000	20 000	35 000
Electrolytic manganese (99% Mn)	8 000	16 000	30 000
Ferro-tungesten (70% W)	7 000	14 000	27 000
Ferro-molybdenum (70% Mo)	1 500	3 000	5 000
Ferro-vanadium (50% V)	1 000	2 000	3 000
Others	2 500	5 000	10 000
Total	125 000	250 000	465 000

A more detailed and separately prepared estimate of the ferro-alloys requirements including the total expenditure involved is given in Table VI.

A pertinent query may be raised that whilst the projected plans for the development of alloy, tool, special and stainless steels and of ferro-alloys have been outlined, what exactly is the current production of these materials in the country. Several industrial licences for the production of alloy, tool, special and stainless steels have been granted and most of the plants are in the process of feverish planning and establishment; as such, it would be difficult to precisely estimate current production of alloy and special steels—the position is rather fluid and rapidly changing. As such, exact present production estimates would not be plausible whilst it may safely be stated the production of alloy steels would be far below 0·1 million tonnes per year at the present stage of planning. So far as the ferro-alloys are concerned, except for the production of different grades of ferro-manganese and ferro-silicon as indicated in Table V, there is hardly any current production of other ferro-alloys although industrial licences thereof have been granted by the Government of India.

Indian raw materials for iron and steel industry

The problems of an iron and steel industry inevitably and continually revolve around its basic raw materials, production techniques, operational skill, efficient plant maintenance, etc. The basic raw materials for an iron and and steel industry are iron ore, fuel, the fluxes, iron and steel scrap, etc. In this review, references will be only made to Indian iron ores and steelmaking quality limestone flux since position of Indian coal and coke is now well known over the last decade or two. For Indian iron ores and steelmaking quality flux, the metallurgical story has unfolded only during the last few years, indicating specifically their deficiencies and remedial measures absolutely essential;[1] the impact of such revelations has been rather sudden but it goes to the

TABLE VI Detailed requirement of ferro-alloy

Ferro-alloys	Price (in Rs) per tonne	Of 100 000 T/Yr of special steels	Of 375 000 T/Yr of special steels	Of 500 000 T/Yr of special steels	Of million T/Yr of special steels	Cost of ferro-alloys in rupees, millions			
	0	1	2	3	4	1	2	3	4
(a) To be manufactured by alumino thermic process									
(1) Ferro-vanadium (50% V)	40 000	150	650	800	1 500	3·000	13·000	16·000	30·000
(2) Carbon free ferro-chrome	4 500	500	1 000	1 500	3 000	2·250	4·500	6·750	13·500
(3) Ferro-titanium	3 126	50	200	300	500	·156	·625	·931	1·563
(4) Ferro-boron	9 450	15	50	70	120	·142	·472	·662	1·134
(5) Ferro-zirconium	2 920	15	50	70	130	·044	·146	·204	·379
(6) Chromium metal	—	30	100	140	250	—	—	—	—
(7) Manganese metal	—	30	100	140	250	—	—	—	—
Sub-total		790	2 150	3 020	5 750	5·592	18·743	24·554	46·576
(b) By electro-thermic process									
(1) Ferro-chromium (high C) (65% Cr)	3 000	4 000	16 000	24 000	48 000	7·800	31·200	46·800	93·600
(2) Ferro-chromium (LC) 65% Cr	4 500	6 000	25 000	36 000	70 000	17·550	73·125	105·300	204·750
(3) Ferro-manganese (80%) (LC) (Mn)	4 000	850	3 200	4 800	8 500	2·720	10·240	15·360	27·200
(4) Ferro-tungsten (70% W)	20 000	1 300	5 000	7 000	14 000	18·200	70·000	98·000	196·000
(5) Ferro-molybdenum (75%)	23 000	250	950	1 500	2 500	4·025	15·295	24·150	40·250
Sub-total		12 400	50 150	73 300	143 000	50·295	199·860	289·600	561·800
(c) Being manufactured in the country									
(1) Ferro-silicon (50%)	1 000	2 600	15 000	25 000	48 000	2·600	15·000	25·000	48·000
(2) Ferro-manganese (75%)	1 000	800	3 500	5 000	10 000	·800	3·500	5·000	10·000
Sub-total		3 400	18 500	30 000	58 000	3·400	18·000	30·000	58·000
(d) Cannot possibly be manufactured No indigenous supply									
(1) Nickel pellets (99·8% Ni)	8 300	3 000	11 000	15 000	30 000	24·900	91·300	124·500	249·000
(2) Cobalt pellets (98% Co)	25 000	25	80	125	300	·625	2·000	3·125	7·500
Sub-total		3 025	11 080	15 125	30 300	25·525	93·300	127·625	256·500
(e) Electrolytic Manganese (95% Mn)		2 500	6 000	8 000	15 000				
Grand total		21 115	87 880	129 445	252 050	84·812	330·403	471·789	922·876

Estimates drawn up by the Ferro-alloys Group based on current prices of ferro-alloys.

credit of all concerned that the acceptance of remedial measures formulated on the basis of painstaking laboratory and pilot plant scale researches undertaken at the National Metallurgical Laboratory, has been equally quick. Details of these metallurgical research investigations and their economic implications were discussed at the International Symposium on Iron- and Steelmaking with special reference to Indian conditions held at the National Metallurgical Laboratory in February 1963[2].

Iron ores

Despite somewhat opposing views, it has now been acknowledged in responsible quarters that Indian iron ores to be classified as one of the classic rich iron ores of the world may not be wholly plausible in a strictly metallurgical sense. The metallurgical characteristics of a classic rich iron ore will basically depend on the nature and characteristics of the ingredients constituting its gangue and the latter's physical mode of distribution and structural association with metallic values of the ore and the gangue's selective presence in different ore size fractions. The gangue content of some of the Indian iron ores resides in the finer ore fractions, such as in —½″ which under the heavily mechanised iron ore mining conditions now introduced in India can constitute between -½ of the total iron ore thus mechanically extracted. The full impact of the problem with which India is faced with relation to the release, storage and utilisation of the masses of iron ore fines to be mined during our successive Five Year Plans will multiply to a magnitude that it will defy scientific solution unless adequate attention is focussed on this important subject and effective steps are introduced to utilise such iron ore fines. Table VII gives some data on the projected developments in iron ore requirements for home use and export.

The above classification is based on expected output of 40–41 million tonnes a year of iron ore for domestic consumption and 25 million tonnes a year for export by 1970–71. It is, therefore, stressed that utilisation of iron ore fines has to be rationally and comprehensively examined for exploitation of what would one day perhaps constitute the biggest national waste of assets and which no other country is likely to permit in view of the practical availability today of advanced technology for their utilisation.

Indian iron ore fines

Utilisation of iron ore fines in India is complicated by the Indian weather conditions. The subject was quite simple when hand-mining was resorted to and selective mining yielded lump size iron ore materials from which the fines were discarded in situ. However, with the introduction of heavy mechanised mining, separation of the ore fines by manual methods from the lumps cannot be attempted or successfully accomplished. It is thus obvious that all the iron ore fines would thereby be sent to the ore handling and screening plant along with the lumpy material which can cause severe complications under

Projected developments in iron ore requirements for home use and export

(All figures in million tonnes per year)

Year	Steel capacity installed	Iron ore requirements for home use	Home consumption approximate installed capacity at large mines						For export : Kiriburu and Bastar/Raipur, Bailadilla, Goa, etc.
			Rourkela	Durgapur	Bhilai	Tisco	IISCO	Bokaro	
			Barsua	Bolani	Rajhara	Various captive mines	Gua	Largely Kiriburu and new mines Taldih, Meghathaburu and Sasangdah	
1960–61	6·00	9 to 10	2·00	1·00	2·00	3·10	2·00		3·40
1965–66	10·00	19·00 to 20·00	3·50	3·00	4·50	3·50	2·00	Up to 3·00 (from Kiriburu about 1·5 million tonnes fines)	12 million tonnes
1970–71	20·00	40·00 to 41·00	Currently under detailed study for formulating expansion plans						25·00 million tonnes

Indian conditions of heavy tropical rain. It has been the experience in India of the steel plants that under Indian tropical weather conditions, the screening and the handling systems become completely blinded and choked due to the muddy conditions caused by the action of tropical rain on the admixture of iron ore fines with the lumpy material. It is in this context that the the entire subject would have perhaps assumed somewhat less significance and importance, had it not caused serious difficulties and plant dislocations in ore handling and movement caused by blinding of the screens during heavy monsoon rainy weather.

In the absence of suitable ore handling, screening and beneficiation methods to prevent the blinding of the screens, such as through wet screening and scrubbing the iron ore followed by dewatering classifier treatment (the slime containing at times up to 24–40% insolubles), a modern ore handling and screening plant involving capital outlay of several crores of rupees can be ultimately even though majestically brought to a standstill. As such, the establishment and operation of a sinter prodution plant which naturally consumes these iron ore fines, is seriously hindered, if not altogether blocked. It is thus of paramount importance that all avenues should be explorated (1) to separate the fines from the lumpy iron ore materials both in fair and rainy weather and (2) to utilise the iron ore fines thus separated to the maximum national advantage for home smelting. Comprehensive investigations have been undertaken at the National Metallurgical Laboratory on pilot plant beneficiation investigations on Bolani iron ores for Durgapur Steel Plant, Barsua iron ores for Rourkela, Kiriburu iron ores for the National Mineral Development Corporation, iron ores for the Tata Iron and Steel Works and Rajhara iron ores for Bhilai Steel Plant, etc. Further investigations will cover iron ores from Bailadilla, Taldih, Sasangdah and other captive mines of Hindustan Steel Limited and of private sector steel plants in the country.

Perhaps the most important method of utilisation of iron ore fines is the use of sinter including self-fluxing sinter. The use of sinter in iron smelting both of self-fluxing or non-fluxing is no longer a field merely of academic interest presenting any unusual features that are today unknown. All the world over, iron production plants are operating with as much as in most cases 100% sinter charge with considerable increase in iron productivity based on low fuel rates. These sintering techniques utilise almost the entire iron ore fines released during mechanised mining and offer acceptable solution in two ways : one being the effective utilisation of the iron ore fines which otherwise will present serious disposal and storage problems and the other, effectively increasing the metal iron output by extracting the metallic values of the ore fines, involving reduced fuel rates through the medium of sinter. It stands to reason that of 100 units of mechanised mined iron ore, if 40 units of iron ore fines are to be discarded, the cost of mining operation will be high. It is therefore necessary from considerations based on cost of mining alone to utilise these 40 units of iron ore fines by all possible techniques acceptable under Indian conditions of weather and operational facilities.

Even where ores of good quality are available, such as in the U.S.S.R., sinter production is resorted to to ensure ores of uniform quality and yield a self-fluxing burden to the blast furnace. In the case of lumpy iron ores being fed into the blast furnaces in India during rainy season, considerable amounts of iron ore fines tenaciously adhere to the ore lumps. If these iron ore fines are removed from the lumpy material by simple treatment such as washing and scrubbing and wet screening, the lumpy iron ore materials would present to the blast furnace maximum burden permeability yielding increased productivity.

Research investigations undertaken by the National Metallurgical Laboratory during the last few years have undoubtedly aroused the interest of Indian iron and steel industry in not only fully appreciating the desirability but also the scientific necessity of adopting optimum beneficiation techniques in the context of Indian weather conditions coupled with characteristic nature and quality of Indian iron ores being exploited. It has been shown that a sinter plant operating with unbeneficiated iron ore fines will not yield the performance expected of it. This is distinctly apart from the position that even should it be possible to handle and screen natural iron ore fines in Indian rainy weather, the sinter produced from natural untreated iron ore fines will be metallurgically of little value in terms of increased iron productivity, lowered coke and flux rates apart from ensuring smooth and hanging-free furnace operations. It is not merely necessary to produce sinter at any cost and of any grade but in order to obtain from its use full iron output potential, it should be of a good metallurgical grade with distinct well established benefits arising through its application. It should also be borne in mind that it is necessary to incorporate return sinter fines in the sinter mix, which following also requisite additions of high-ash coke breeze will make the acid contents (alumina and silica combined) abnormally high in cyclic sinter feeds. Such successive incorporation of return sinter fines in the sinter mix made up of unbeneficiated ore fines, will continuously build up the acid contents of the sinter feed to an alarming extent which in cyclic operations will render the resulting self-fluxing sinter to be of poor physical strength and metallurgical value to be acceptable. These undesirable factors exercise cumulative deteriorating effects when the sinter plant goes into continuous production yielding weak, friable and poorly reducible sinters made out of unbeneficiated iron ore fines.

Limestone (steelmaking quality)

Limestone is the important flux used in iron and steelmaking. When the steel output in India was small, limestone with less than 5% insolubles could be obtained. With the heavy demands of the expanding iron and steel industry both in the public and private sectors on limestone, the quality of the latter has deteriorated rapidly with insolubles therein rising to 12–13%, causing thereby heavy deficiencies in the fluxing power of the limestone for steelmaking turning it into 'slag making' both literally as also metaphorically. Realising the importance of the subject the National Metallurgical Laboratory has during the last few years undertaken series of investigations for optimum economic beneficiation and agglomeration of limestone for steelmaking. For limestone to be used as metallurgical flux in steelmaking, maximum availability of base CaO is necessary and for that purpose, silica content of the limestone should be low so that its CaO base is not used up in fluxing its own silica at the expense of the acids arising out of the oxidation of metalloids in a steelmaking bath, such as silica and P_2O_5 whichhave, of necessity, to be fluxed into the slag. Limestone for use in steelmaking should contain very low silica contents preferably of the order of 1–2%, even though the open-hearth grade Indian limestone is specified to contain not more than 6% acid insolubles, corresponding to about 7·5% total insolubles. The quality of the Indian limestones used in steelmaking vis-a-vis their silica content is deteriorating and the insolubles in limestone for steelmaking are now of the order of 12–15%. With these poor grades of limestone, production in the steel plants can be adversely affected apart from the operational difficulties arising, such as of poor heat-exchange between the furnace gases and the steel bath causing damage to the furnace roof thereby, high consumption of the limestone itself in order to meet the flux needs of the acids resulting from the oxidation of metalloids, danger of reversion of phosphorus from slag to metal during steel-refining due to lack of stabilizing base in the slag and dangers of off-heats, etc. The limy slag covers itself is a good heat insulation over the molten metal bath and with increase in its thickness, the inadequacy of effecting maximum heat-exchange so necessary in open-hearth steelmaking, will become apparent causing loss of steel output and higher production costs, heavy maintenance expenses, etc. ; the cumulative effects of these factors can be far more adverse than is fully realised. Limestone used for calcination to yield burnt lime is specified to contain a total of 10% acid insolubles corresponding to 12% total insolubles. The burnt lime is also used in the open-hearth steelmaking to meet inevitable deficiencies of the base CaO during refining stages of open-hearth steelmaking. If, however, through suitable limestone beneficiation, silica contents of the limestone can be reduced to about 2%, adequate CaO base would thus be available and as such, addition

which would naturally mean savings in the flux costs considering that the burnt lime costs approximately three times that of limestonse.

The severity of the problem will be realised when the steel production in India, projected at 20 million tonnes of steel per year at the end of the Fourth Five Year Plan, has to be physically attained; the contrast will become sharper with increasing deterioration in the quality of metallurgical grades of limestone and lack of its adequate indigenous resources. It would therefore be appreciated that beneficiation of limestone for steelmaking will become a crucial metallurgical necessity, if not an absolute economic necessity. It has been argued that any industrial application of beneficiation techniques must be based on economic advantages thereby accruing. As such the beneficiation costs have to be adjudged in the ultimate analysis against the lowered consumption of the limestone flux, acceleration in steelmaking following on increased reactivity of the upgraded limestone concentrate, reduced possibilities of off-grade steel heats and less damage to the furnace roof, etc. It will be difficult to straightway evaluate the improved economics resulting from the use of beneficiated limestone at this stage even though there are clear indications thereto. It has been shown in these investigations that the upgraded limestones can be adequately pelletized without expensive binders and the pellets possess adequate strength for handling and providing necessary lime boil in open-hearth steelmaking. An extremely well-equipped and fully integrated Mineral Beneficiation Pilot Plant is currently in full operation at the National Metallurgical Laboratory, with a capacity of treating up to 5 tons of a particular ore per hour depending upon its nature and concentrate needed, involving a capital outlay of Rs 50 lakhs (about a million dollars) during the Third Five Year Plan.

The use of beneficiated limestone in ironmaking in the blast furnace has not been taken up, even though increasingly high ash contents of Indian coke will require in turn additional quantities of the limestone flux. The limestone briquettes required for blast furnace have to be exceedingly strong unless the upgraded limestone which is in the form of fines is directly used for making self-fluxing sinter. The reduction in silica content of the beneficiated limestone for use in iron production will have to be balanced against the high alumina contents of Indian blast furnace slags requiring certain minimum silica values therein[3, 4].

Small foundry iron production plants

The importance of small plants for iron production has been focussed by the National Metallurgical Laboratory through extensive pilot plant trials at the Low Shaft Furnace Pilot Plant; relevant technical results and recommendations were presented at the International Symposium on 'Iron- and Steelmaking with Particular Reference to Indian Conditions' held at the National Metallurgical Laboratory[5,6,7]. The subject has also recently been aptly discussed and well presented by Dastur[3,4] and by Dowding and Whiting[8]. Sir Jehangir Ghandy in one of his Addresses[9] has also aptly presented the scope of small ironmaking and steel plants particularly under Indian conditions.

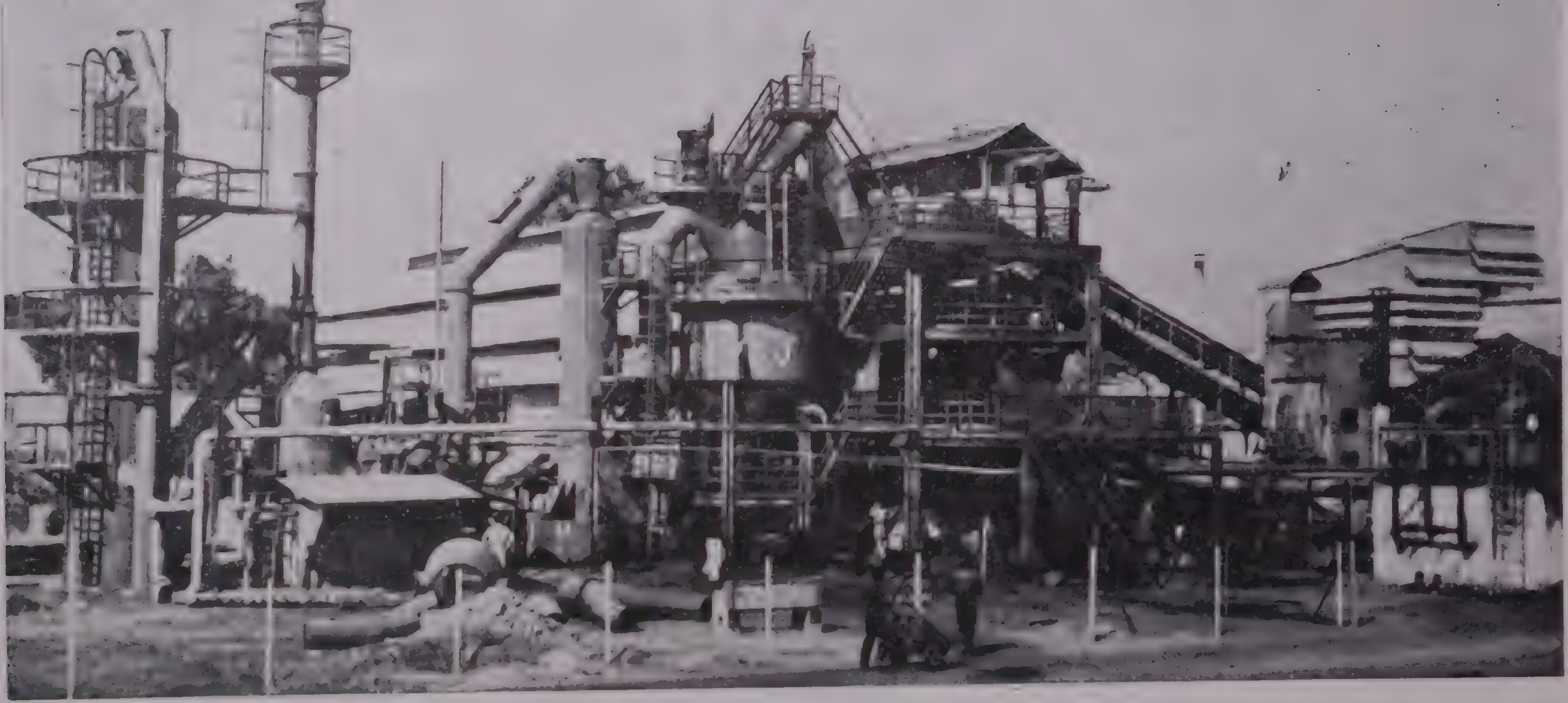
Several industrial licences have been granted for small foundry ironmaking plants in the country based on regional utilisation of raw materials.

In most steel producing countries today, the flourishing of both big and small plants dispersed on the basis of raw materials' regional distribution and transport facilities is often met with. Even in the United States, there are several small plants with an annual capacity of a few hundred thousand tonnes whilst integrated iron and steel complexes of over 6 million tonnes annual capacity do not exceed half a dozen. Likewise in Japan, new small foundry iron plants are currently being established, whilst there are a number of small plants successfully operating besides integrated iron and steel complexes embodying as it were the principle of 'walking on both the legs'. The small plants specifically cater to the regional requirements of premium quality iron production. The explanation that the small plants may be carry over from earlier days is only partly valid since new small plants are also being concurrently established. The parallel growth of integrated iron and steel complexes and small foundry iron plants is a step in the right direction both in advanced and under-developed countries. The total indigenous fabrication of such small plants in India today is a full-scale possibility and would encourage the growth in turn of related engineering industries. The growth of the small ironmaking plants can be based on the use of surplus nut coke from integrated steel plants, or alternative fuels, such as the low temperature carbonized coke or lignite coke made from Neyveli lignite in South India. The industrial scale production of low temperature coke (Kolsit) from Singareni non-coking coals has been well established by Regional Research Laboratory (Hyderabad) of the Council of Scientific and Industrial Research. In extended full-scale trials on iron smelting in the Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory, Kolsit proved an ideal fuel for iron production—equally favourable results were achieved with low temperature coke made from non-coking coals from the Bengal-Bihar basin. The low temperature coke is more reactive than hard metallurgical nut coke which itself is an alternative sub-standard fuel for iron smelting. Foundry iron production through electric smelting is also feasible in India, as currently projected in Rajasthan and South India where optimum electric power rates are available. The above possibilities form the basis for the grant of industrial licences for foundry iron production in the Punjab, Andhra Pradesh, Rajasthan, Maharashtra (Western India), Goa, Orissa, etc. whilst similar installations are being actively considered in Gujarat. Likewise, small foundry iron blast furnaces attached to the integrated Hindustan Steel plants as 'satellite' installations are also being currently considered. A small foundry blast furnace with the minimum of mechanisation of 100 tonnes daily output, with 2/3rd of its cleansed gas bleeding and sand bed casting has been most successfully and economically operating in India at Barbil (Orissa) for the last several years, originally established with a capital outlay, including housing and land, of about Rs 250 per annual tonne of iron. It would indeed be hard to put up a big blast furnace today for foundry iron production on identical capital outlay per annual tonne of iron.

A modern high output giant blast furnace with all its latest ingenious and expensive auxiliaries, is intrinsically a highly capital intensive unit; more so, if its capacity is utilised merely to produce a relatively low cost, intermediate and crude product viz., foundry pig iron. Thus to utilise the giant blast furnace with its high initial capital investment and overheads of heavy, integrated iron and steel complex for foundry ironmaking may in most cases not be altogether acceptable on economic grounds; in the ultimate analysis, however, it would be tantamount to producing a crude semi-finished product in a heavily capitalised integrated iron and steel complex, instead of giving the same crude semi-finished product its logical steel product-mix, which would thereby effectively ensure maximum capital returns and dividends on the heavy capital investment made. Thus, any foundry iron made in a heavy iron and steel complex would in most cases be at the expense of corresponding if not greater output of steel and its finished high premium product-mix, yielding thereby unfavourable capital returns. It is hardly necessary to indicate that integrated iron and steel bases are normally well balanced complexes. At the same time it is well known today that blooming rolling-mill capacity is normally kept well in surplus in relation to iron- and steelmaking potential in a modern, integrated iron and steel plant; this flexibility would enable the operation of the blast furnace plant exclusively on basic iron for steelmaking. In this country, integrated steel plants have hitherto supplied the major foundry pig iron requirements of engineering industries. Prior to last World War II, however, the spread over of the demands of steel end-products did not follow any uniformly planned or steady patterns thereby making room for switching over of ironmaking capacity from basic to foundry grades of pig iron. The situation has today undergone radical changes, amply justifying the stand that the responsibility for foundry ironmaking should progressively and exclusively pass on to non-integrated blast furnaces.

World-wide trends in general favour the production of foundry iron in relatively smaller blast furnaces. In India, the reserves of metallurgical grade coking coals are extremely poor, estimated at about 1 500 million tonnes.[10] The operations of big blast furnaces are dependent upon the use of optimum sized good grade metallurgical coke home made or imported. It is thus emphasised that big blast furnaces should be used for making only basic iron to be refined into steel and finally processed into specific product-mix, whilst the smelting of foundry iron ought to be undertaken in comparatively smaller blast furnaces which can operate on alternative Indian fuels referred to earlier. Such measures would be metallurgically feasible and economically acceptable and from the standpoint of highly scanty proved reserves of indigenous metallurgical fuels, perhaps offer the only solution both on short-term and long-range basis. The opportunity thus exists of bridging the present gap between the demand and supply of foundry grades of pig iron and of ensuring additional supplies for the future, independently of integrated iron and steel bases currently in operation or those planned.

India is a land of long distances involving heavy rail freight costs which can more than off-set any increase in the iron production costs in small regionally dispersed foundry ironmaking units; the latter can well pattern the in-tandem growth of medium and light engineering industries region-wise, over a thousand miles away to the north and south of the major Indian integrated steel plants located today in the Bengal-Bihar-Madhya Pradesh belt. This then depicts the general Indian pattern of foundry ironmaking in small plants in the broad spectrum covering the growth of iron and steel industry in India since the last World War. The subject has been critically discussed at different platforms in India and abroad by various authors[11,12] including the



3 *The Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory.*

International Symposium on 'Iron and Steelmaking with Particular Reference to Indian Conditions' held at the National Metallurgical Laboratory in February 1963 and earlier in February 1959 on 'Iron and Steel Industry in India'. Figure 3 shows the Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory which has produced several thousand tons of foundry grades of pig iron from regional raw materials from different parts of India since it went into operation in February 1959. The results obtained on the metallurgical feasibility and economic acceptability of iron smelting with regional raw materials in the Low Shaft Furnace Pitot Plant have been very valuable in determining the growth pattern of foundry iron production in small plants.

Conclusions

Fast developing countries such as India have fully realised the importance of well-knit and integrated iron and steel bases to feed the chain-reaction growth of secondary and processing engineering industries that in turn form the backbone of consumer industries catering to the multitudinous needs of diverse products essential both in times of war and peace. Whilst the iron and steel industry is highly capital intensive, no country can afford to leave it to the vagaries of international trade. The rise of such an industrial developing economy in underdeveloped countries, would however provide the basis subsequently of growth on 'one's own legs' and not an alien superstructure based on the imports of iron and steel that is unlikely to withstand the stresses of peace and least of all the strains of war. The establishment of home iron and steel industry provides in the ultimate analysis a self-sustaining economy to assist a fast developing country, such as India, to the stage of an economic 'take-off'.

Such growth pattern of iron and steel industry in India in her economic development Five Year Plans has not been without its inevitable fate of sweat and toil through which India is passing in its steady yet sure march in not only attaining self-sufficiency in iron and steel but also in her ultimate objective of becoming a leading iron and steel producing country in the world.

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Scope and Function of the Regional Foundry Station of the National Metallurgical Laboratory at Batala

R. M. Krishnan
B. R. Nijhawan

THE idea of establishing Regional Foundry Stations was first proposed by Sir Jehangir Ghandy, Chairman, Metals Committee and Executive Council of the National Metallurgical Laboratory, who while complimenting the National Metallurgical Laboratory for the valuable research and development work underway on foundry sands and bonding clays, suggested at the Metals Committee meeting the formation of Regional Foundry Stations to give technical assistance to so many of the small foundries which cannot otherwise afford independent testing facilities nor technical personnel for the evaluation of foundry sands and other moulding materials. This proposal gathered further momentum when the Foundry Productivity Team sponsored by the National Productivity Council after the visit to Sweden, USA and Japan strongly recommended the establishment of Regional Foundry Stations at important foundry centres to make available testing facilities to small foundries. The Board of Scientific and Industrial Research and Governing Body of the Council of Scientific and Industrial Research finally endorsed this proposal for establishing four Regional Foundry Stations and asked the National Metallurgical Laboratory to formulate plans for setting up four Regional Foundry Stations for providing technical service facilities to the foundries.

The first Regional Foundry Station set up by the National Metallurgical Laboratory in the industrial estate, Batala, Punjab was declared open on 10th April, 1964 by Hon'ble Mohan Lal, Home Minister, Punjab, in the midst of over 500 foundry industrialists from all over Punjab State and other parts of India. This is the first of the four Regional Foundry Stations to be set up by the National Metallurgical Laboratory to study the problems of foundries and give them necessary technical assistance and operational guidance.

Speaking on the occasion, Dr S. Husain Zaheer, Director-General, Scientific and Industrial Research, said that one of the objectives, if not the only objective, of the Council of Scientific and Industrial Research would be to assist the industries—new industries and old industries—by bringing to them the latest improvements in science and technology pertaining to their particular field. The National Metallurgical Laboratory, Dr Zaheer said, has established a very high international reputation for the high quality of its work. While the work being done in the different centres may be very good and even admirable, it is necessary, Dr Zaheer pointed out that technicians and scientists must go out with the latest knowledge and improvements to the centres of industry and sell their knowledge so that it is properly applied

Cupola operator in a foundry at Batala being shown the method of forming a tap hole by the Field Staff of Regional Foundry Station.

Mr R. M. Krishnan, Assistant Director; Dr B. R. Nijhawan, Director; National Metallurgical Laboratory.

Defects in a casting being examined in a local foundry at Batala by the Field Staff of Regional Foundry Station.

and used. Based on this concept and objective of the CSIR, the NML has come forward to set up Regional Foundry Stations to spread the good deal of knowledge the NML has collected in foundry science. The first Regional Foundry Station has been established at Batala and this has been largely due to the enthusiasm of local foundries and the assistance given by the State Government, Dr Zaheer said. On behalf of the CSIR, Dr Zaheer expressed his gratitude to Sardar Pratap Singh Kairon, the Chief Minister of Punjab, Hon'ble Mohan Lal, Home Minister, Punjab and the foundry industrialists in Punjab for the valuable assistance they had given in establishing the Regional Foundry Station at Batala. Concluding, Dr Zaheer said he was absolutely confident that with the enthusiasm and the great vigour of the industry and the industrialists in the area, this first Regional Foundry Station at Batala will be utilised to its fullest extent to derive maximum benefits to the industry.

Mr Mohan Lal, Home Minister of Punjab State, while inaugurating the Regional Foundry Station, said that it was a very proud occasion not only for Batala but also for the Punjab State and expressed the hope that the industrialists of Batala and in Punjab would set an example for the rest of the country by utilising the facilities the maximum extent and thus improving the quality of their products. Mr Mohan Lal further said that it was up to the industrialists and workmen to keep pace with the latest developments and unless this was done, they were bound to be left behind in the race. He hoped that the industrialists will fully realise the value of this station and would justify the selection of Batala as the site for locating the first national foundry station.

Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, in his welcome address, thanked the distinguished guests, foundry executives and foundrymen for their full co-operation and also expressed his gratitude to Sardar Pratap Singh Kairon, Chief Minister of Punjab for the keen interest shown by him and to Mr Mohan Lal, Home Minister, Punjab, and Dr S. Husain Zaheer, Director-General, Scientific and Industrial Research, for participation in the function. He also complimented the staff of the Regional Foundry Station for the hard work put in by them under the very active guidance of Mr R. M. Krishnan, Assistant Director of the National Metallurgical Laboratory. He announced that the testing facilities will further be expanded and would also include melting units to enable the station to undertake experimental work on metal melting. The Regional Foundry Station, Dr Nijhawan said, will be at the total disposal of the foundries in Punjab for providing technical assistance at site as well as to introduce scientific control methods in their foundries.

Equipment and facilities

The Regional Foundry Station has been equipped with adequate facilities for testing of foundry sands and bonding clays for routine control of sand mixtures, as well as to find out their suitability for use for foundry moulding purposes. The station has also been equipped to undertake the analysis of both ferrous and non-ferrous metals and also for carrying out chemical analysis of moulding sands, etc. In the second phase, it is proposed to expand the service facilities to enable the station to undertake metallography and mechanical testing of metals and alloys and will also be equipped with necessary melting units for undertaking experimental work on problems relating to metal melting. The station has a small library which will be gradually expanded to provide facilities for technical reference on diverse fields of foundry technology.

New horizon for the cast metal industry

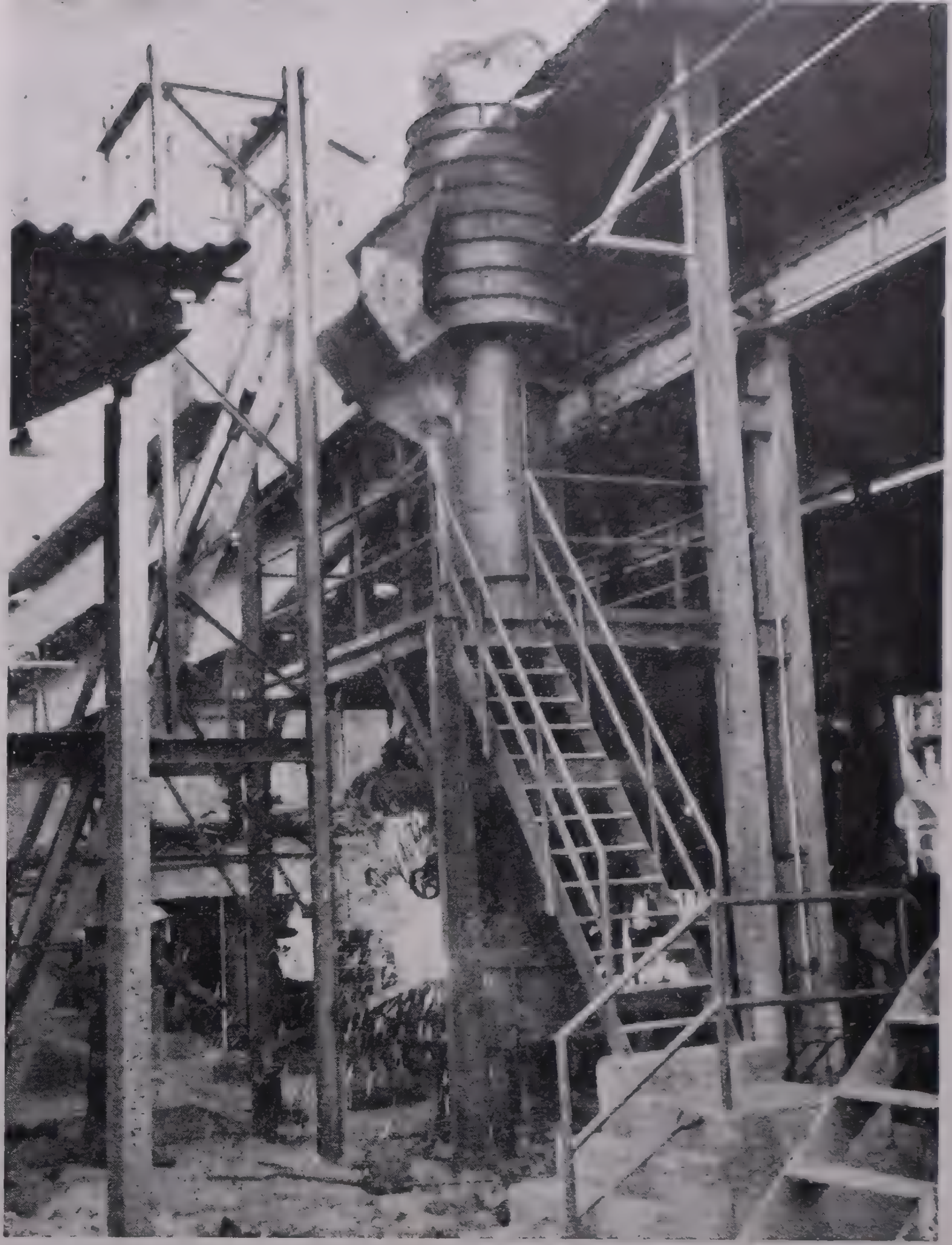
With the development of basic and heavy engineering industries under the stimulus of the Five Year Plans, a new horizon has opened for the cast metal industry for not only consolidating the existing foundries in India but also setting the pace for development of malleable iron and light alloy foundry industry for the production of casting for automobile and aircraft industries.

During the last decade, there has also been a distinct change in the pattern of development of foundry industry in India as new foundry units with better plant layout have been set up almost at the rate of about 3 units per year for the production of quality castings to meet other engineering industries. There is also a powerful trend towards mechanisation and modernisation of the existing units apart from introducing quality control. The heavy foundry and forge plant now coming up at Ranchi will fill up the lacuna in the production of heavy iron and steel castings weighing up to 100 tons per piece.

Foundry industry today

There are at present more than 2 000 foundries producing non-ferrous, iron, steel and malleable iron castings. In the high duty iron field, for many years, meehanite castings have been produced in India under licence from the Meehanite Corporation for chemical, automobile, machine tool, sugar mill, crane parts, etc. The malleable iron foundry industry is still in its infancy although the potentialities for large scale developments of this branch of industry are rated high. The steel foundry industry, although relatively of a later development, has made considerable progress in the use of most modern foundry practice and production of quality castings in some of the foundries. The production of high grade and special steel casting is, however, yet to be developed on a large scale. In the field of light alloys, production of aluminium alloy castings is quite significant as compared to the family of other light alloys.

In the field of non-ferrous castings, Railways are the major consumers as nearly 3 000 tonnes of bronze castings and 6 000 tonnes of anti-friction alloys are at present consumed in the locomotive and rolling stocks of the Indian Railways. There are about 100 foundries engaged in the production of industrial castings for use in railway and other industries and about 10 per cent of these foundries can produce castings according to specification. It can be stated that non-ferrous foundries in general and particularly those producing commercial utility castings are scattered throughout the country.



Tapping of pig iron from 5–6 tons/day capacity vertical shaft furnace having provision for fuel injection, designed and fabricated at the National Metallurgical Laboratory.

Development in the Third Five Year Plan

The Third Five Year Plan conjures up the creation of 1 40 000 tonnes of additional capacity for grey iron castings in the public sector alone. The production of steel castings which is currently estimated to be about 40 800 tonnes will be raised to 52 000 tonnes by 1965-66 and is also proposed to have an additional capacity of 76 000 tonnes in the public sector plant at Ranchi, Durgapur, Chittaranjan and the foundries attached to new steel plants. The estimated annual demand for malleable iron castings is also likely to go up to 36 500 tonnes by 1965-66.

Raw materials

Availability of the right type of raw materials has an important bearing on the development of foundry industry. The chief raw materials required for the foundry industry are pig iron, hard coke, good quality steel scrap, non-ferrous metals and alloys and scrap, foundry moulding sands, bonding clays and ancillary binders, etc. While the basic materials such as iron ore, coal and other mineral ores are in good reserve, perhaps the chief bottleneck in the production of finished products is the short supply of foundry grade pig iron to meet the heavily increasing demand of India's foundry industry; this factor is affecting the other basic industries in turn. The demand for foundry grade pig iron is currently estimated between 2–2·5 million tons against the estimated production of 1·23 million tons during 1962-63.

Industrial complex in Punjab

Punjab has emerged since independence as the home of small entrepreneurs. The number of registered factories in 1947 was not more than 600. During the last 15 years, the industrial sector has shown striking development with about 4 000 factories registered. Broadly the composition pattern of industrial complex in Punjab is similar to that in the country as a whole with agriculture and live stock based industries accounting for the major part of the industrial employment and output followed by engineering. It has about 11 large and medium scale units and in small scale sector, Punjab has 250 units manufacturing machine tools and accessories out of the total of 350 units in the entire country manufacturing machine tools without any foreign collaboration.

SAND TESTING LABORATORY

An experimental sand mix being prepared at the Regional Foundry Station.

Pattern and distribution of industrial units in Punjab

The striking feature of the industrial pattern in Punjab is the predominance of small size units. There are nearly 25 000 small industrial units in the State providing light engineering products like machine tools, sewing machines, bicycles, fans, radios, surgical instruments and components, spare for textile machinery, domestic utensils and a variety of the other consumer goods. Heavy industries such as manufacture of large cranes, locomotives, automobiles, etc. do not exist in the State.

The engineering industries are spread over the entire State with certain centres gaining prominence in certain specialised trades like Ludhiana for cycle products and sewing machine industry, Batala and Jullunder for agricultural implements, Ambala for scientific instruments, Jullunder for brass and pipe fittings and Jagadhri for non-ferrous castings, etc. The industrialisation of the State has further been augmented by the setting up of 6 industrial estates at Ludhiana, Sonepat, Nilokeri, Batala, Mallenkotulu and Nabha, which are becoming great industrial centres. Further, 14 more industrial estates and 10 development colonies in urban areas and 72 industrial estates in rural areas are proposed to be set up in the State.

There are more than 700 foundries in Punjab located mostly at Batala, Ludhiana and also at Ambala, Faridabad and Amritsar. Batala is fast becoming a centre for the manufacture of machine tool castings and agricultural implements and Ludhiana for machine tools, diesel engines, presses and other machines.

There are only two steel foundries : one at Faridabad and the other in Jullunder city. It is reported that three steel foundries are under construction : one each at Jullunder, Ludhiana and Patiala. Two more steel foundries are expected to come up : one at Faridabad and the other in Yamunanagar. It is also worth mentioning that perhaps Punjab is the only State to put up a steel foundry for the manufacture of steel castings.

Problems facing the foundry industry in general

The problems facing the foundry industry can be broadly summarised as follows :

(1) Lack of adequate and regular supplies of the essential raw materials such as foundry pig iron Gr. I and II, graded scrap for steel melting and low phosphorus pig iron for the malleable iron industry.

(2) Lack of adequate supply of processed raw materials like high quality silica sand, bonding materials, core oils and binders, etc.

(3) Inadequate development of ancillary industries to supply according to specification the various items for the foundry industry such as chaplets, moulding boxes, pins and bushes, etc.

(4) The high ash content of coke which necessitates the employment of high fuel ratio as well as the difficulties experienced in getting adequate supplies of coke in different regions of the country.

(5) Lack of adequate pattern-making capacity, especially metal patterns and core boxes for mechanised foundries for mass produced items.

(6) Lack of easy availability of foundry equipment and machinery from indigenous sources.

(7) High inventory of foundry raw materials and spare parts due to the difficulties in getting regular supplies.

(8) Lack of trained technical personnel both at supervisory and non-supervisory levels.

(9) Lack of proper incentives based on well-planned schemes by which wages can be linked up with production.

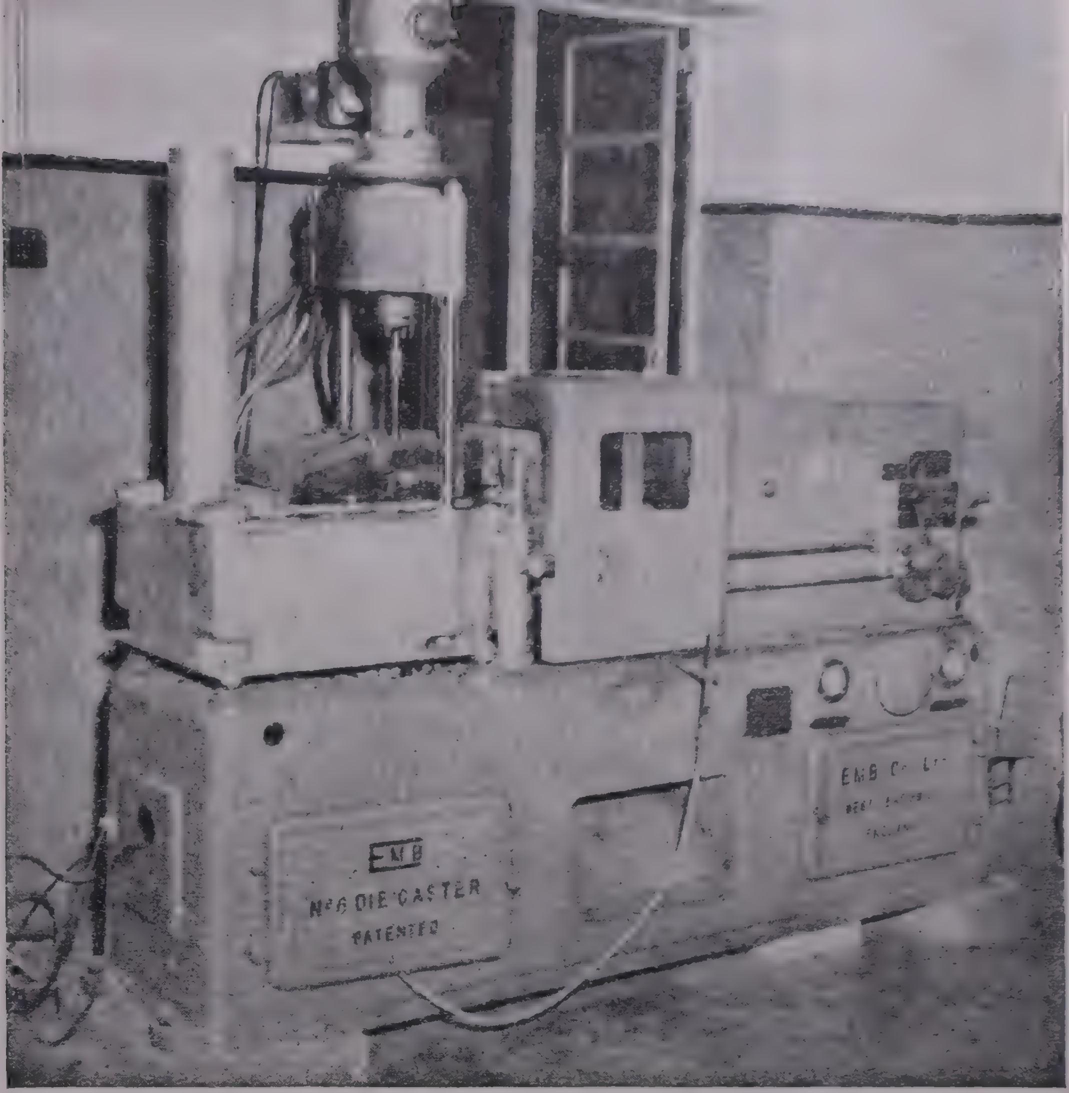
(10) Lack of adequate testing facilities.

(11) The general average deficiency in application and control of process details.

Programme of work of Regional Foundry Station

The tentative programme of work envisaged for the Regional Foundry Station will be as follows which will be implemented in a phased programme :

(1) Periodical testing of foundry sands, bonding clays used in foundries and raw materials used for



A view of the Die-Casting Unit installed at the National Metallurgical Laboratory.

melting like pig iron, limestone, coke, etc. as well as finished products.

(2) To tender technical advice regarding selection and application of indigenous foundry sands and other moulding materials including selection of metal charges for the production of various types of castings.

(3) To undertake ad-hoc investigations on the problems faced by individual foundries and to suggest suitable remedial measures thereof.

(4) To conduct a regional survey of the moulding materials available in those regions and to conduct complete study of the chemical and physical properties of the moulding materials.

(5) To conduct periodical refresher courses to the staff sponsored by the foundries.

(6) Standardisation of melting and moulding techniques in under-developed foundries.

(7) To advise the operational staff on modern foundry technology and to issue technical bulletins periodically.

(8) To carry on research and development work, standardisation and simplification of moulding, melting and other technological procedures to achieve quality as well as productivity.

Formulation of standard foundry sand for testing

With a view to evaluate the quality of bonding clays and synthetic binders for making foundry sand mixtures for moulds and cores, it is imperative that the foundry industry should have a standard sand of uniform chemical composition, grain shape and fineness available from one natural source. In India, so far no attempt has been made to formulate a standard sand for such testing purpose nor has any efforts been made to examine the known available sand deposits for such use. Keeping this in view, the National Metallurgical Laboratory has taken up this work and the standard specification has been formulated in collaboration with the Indian Standards Institution. Work has also been taken up at the NML Regional Foundry Station at Madras in collaboration with the Madras Public Works Department to find out the suitability of Ennore sand for this purpose so that the standard sand preparation plant for cement testing at Ennore could advantageously be utilised to prepare standard sand for foundry purpose as well.

Survey of high silica sand in Punjab

Considerable deposits of sand are known to exist in Ambala, Rohtak and Gurgaon districts of Punjab. Since a number of steel foundries are proposed to be set up in Punjab during the Third Five Year Plan, it is imperative that a comprehensive survey should be carried out to assess the available resources of high silica sands which can be used for moulds and cores in the steel foundries that will be set up. Preliminary investigation work has already been initiated on various sands received from the State Geology Department, Punjab, and the results of the investigations so far carried out have been made available to the Department of Industries, Punjab. It is proposed to intensify the efforts during this year so that the known deposits of silica sands can be fully investigated.

A view of the Shell Moulding Unit installed at the National Metallurgical Laboratory.

Research and development work at National Metallurgical Laboratory

Till recently, Indian foundries did not have at their disposal adequate data on foundry moulding materials of the country which are very essential for the production of quality castings. The NML, since its inception, undertook a comprehensive study of Indian foundry moulding sands and bonding materials to assess their moulding characteristics and to determine their suitability for various types of castings. Samples of foundry moulding sands and bonding clays were obtained from many sources and detailed questionnaires were sent out to important foundries in India to elicit data relating to the foundry sands used by them. A large number of sands from localities all over India were investigated including study of their properties and suitability for different types of casting jobs. Over fifty different types of moulding sands were studied which included natural moulding sands, bank sands and dune sands which are obtained from river beds, sea coasts, dunes, high silica sands and special sands like zircon sand, etc. Results of the investigations carried out in the Laboratory `have been of immense value to the foundry industries in selecting the proper types of sands and bonding clays for their different types of castings. One of the most modern and biggest steel foundries of the country at Jamshedpur has set up its sand processing unit based on the investigations done at NML. Similar investigations were also conducted with bonding clays (numbering over 20) like bentonites for the preparation of synthetic sand mixtures for various types of castings.

A monograph entitled 'Foundry Moulding Sands of India' covering the extensive work done in the National Metallurgical Laboratory on foundry moulding sands and bonding clays has already been published and has been reviewed at home and abroad as a monumental work of considerable value to the foundry industry.

The National Metallurgical Laboratory has also investigated bentonites received from Germany, Spain, UK, Poland, etc. under the International Programme of the Working Group for Bonding Clays.

Besides the exhaustive studies carried out on foundry moulding sands and bonding clays, a large number of investigations on behalf of public and private sector industries have been conducted on the melting and casting problems of metals and alloys. To cite an example, super duty aluminium bronze castings of tensile strength of the order of 60 kg/mm^2 and minimum elongation 20 per cent are required for 25 kV traction overhead equipment in Indian Railways Electrification Project. At the instance of the Research, Designs and Standards Organisation, Ministry of Railways, the work was taken up to standardise the methods of melting and castings in detail so as to meet the specification laid down by the French Consultants for the Railway Electrification Project so that the railway workshop can undertake the casting of such alloys. The procedure to be employed for melting and casting to get the desired properties was worked out after thorough investigation and was suggested to the organisation. The work done was commended by the Railway Research, Designs and Standards Organisation (Railway Board) as extremely useful for applications in overhead electrical fittings in their electrification projects.

Aluminium-silicon alloys are extensively used for automobile castings and other engineering applications, Till recently, no single modifying agent has been developed for refining both the primary silicon crystals as well as the eutectic matrix of the aluminium-silicon alloys. At the NML, a new modifying agent has been developed which has been found to remarkably improve the fluidity, machinability and tensile strength of the alloy.

The use of pure iron powder for cutting and flame-scarfing of massive steel castings particularly alloy steel and stainless steel castings employing specially designed cutting nozzles is progressively increasing. Iron powder is also used in the manufacture of iron powder coated welding electrodes. Since the present requirements of iron powder for autogenous cutting in India are met entirely by import, a suitable process has been successfully developed at the National Metallurgical Laboratory and the technical know-how developed has been released to industry for industrial scale production on payment of premia-royalty basis.

Iron smelting plant for Punjab

In East Punjab alone, there are over a hundred iron foundries centred round Batala whose requirements of foundry grade pig iron have to be obtained chiefly from Bihar region, thus entailing transport over long distances and delay in getting supplies.

Based on the feasibility report of the smelting trials conducted in the Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory with the iron ore of Mohindergarh area, non-conventional fuels and suitable fluxes, it is gratifying to note that Government of Punjab have taken up the project to instal an iron smelting plant of 100 000 tonnes per annum to meet the progressively increasing demands of foundry grades of pig iron for foundries in the Punjab. The consultancy and installation work have been taken up by Messrs Ashmore, Benson, Peace & Co. Ltd., England (Member of the Davy Ashmore Group).

Collaboration with national and international organisations

The National Metallurgical Laboratory is today acting as a nucleus for many of the long range and short-term projects connected with the metal and mineral industries, which are being referred to this Laboratory in increasing numbers by establishments in both public and private sectors. Long range fundamental work has also been done for making the best use of foundry raw materials and to evolve national standards. In this connection, it is pertinent to record the appreciative remarks made by the Chairman of the Foundry Sectional Committee of the Indian Standards Institution, who placed on record the services rendered by the NML to the industry in making the best use of foundry raw materials and for formulating national standards for foundry silica sand, bentonite for use in foundries, graphite for use as foundry facing material, natural moulding sand, silica fluor for use in foundries, method of test for foundry core oils, formulation of standard sand for use in foundries, etc. With technical and professional associations like the Institute of Indian Foundrymen, Indian Institute of Metals, etc. active co-operation is maintained in diverse fields of foundry technology.

Conclusion

It is a common observation that whereas research is often pursued to brilliant conclusions, applications of its results can be demonstrated only by the industry. As such throughout the world this concept is being implemented to step up scientific and academic activities designed to promote the applications of industrial research. It is also well known that there is no one distinct known way to calculate the returns from a programme of pure reseach until its processing has been completed through technological applications which can often take a long time. The foundry industry fits in admirably well in such a pattern as it takes the responsibility of closely studying the progress of pure research for the applications of potentially useful results in its various aspects relating to ferrous and non-ferrous metals and alloys. The foundry industry needs, therefore, fundamental as also technological research to accomplish these basic objectives.

It is a happy augury that Batala has taken the lead in the drive to export 36 000 tons of cast iron soil pipes a year to the USA which would result in foreign exchange earnings of about Rs 2 crores. In this and other development fields, the Regional Foundry Station at Batala will be at the total disposal of the foundries in Punjab for improving the quality of their castings as well as to introduce scientific methods of control in their foundries.

The Suitability of Jainti Dolomite for Sintering in Shaft Kilns

P. C. Sen
M. R. K. Rao
H. V. Bhaskar Rao

Sintering and firing characteristics of Jainti dolomite were studied to assess its suitability both as semi-stable and completely stabilised product for use in steel-making refractories. The dolomite was pure and could be used for manufacturing both the products, if suitably processed.

SINTERING and firing characteristics of Jainti dolomite were studied to assess its suitability both as semi-stabilised and completely stabilised product for use in steelmaking refractories. The dolomite occurs[1] in Dalings (Archaean) covering an area of about five square miles in the north-eastern corner of Buxa Duars of Jalpaiguri district of West Bengal, the main source being the Sachhaphy ridge to the south and northeast of Jainti Railway Station, Jalpaiguri. The raw dolomite which was generally ash-grey and rarely white or black, was fine grained and massive with occasional patches of medium grained and saccharoidal varieties. Excepting slight variations in colour at places and occasional intercalations of argillaceous bands, the dolomite was of uniform quality. The dolomite contained many veins of quartz and calcite. The reserve is said to be practically inexhaustable.

Experimental

Chemical analysis of the dolomite was done as per standard method. Mineralogical study was done on thin sections and powder mounts. Differential thermal analysis on raw samples was carried out in a Honeywell Brown apparatus using alumina holder. The rate of rise of temperature as measured from the inert reference material was kept at about 10°C/min. Samples of dolomite 4 in as well as ½ in to 1 in lumps were calcined at 1 620°C and 1 700°C for 3 hours and their physical appearance was studied and porosity and bulk density were determined by hydrostatic balance using kerosene oil. Bulk density was determined by mercury hydrometer also.

Results and discussion

The sample of raw dolomite was of sizes varying from 4 in to 1 in and of grey to whitish colour. Some samples were of dark grey colour. Calcite was observed in some pieces of dolomite in streaks, veins and patches. The chemical analysis of dolomite sample is given in Table I. The analysis of picked samples showing different colours are also given therein.

TABLE I Chemical analysis of raw dolomite

%	Sampled variety	Grey variety	Dark grey variety	Grey and white variety
Moisture	0·10	0·10	0·68	0·08
Loss	46·38	46·67	46·77	44·43
SiO_2	0·80	0·62	0·24	0·87
Al_2O_3	0·33	0·34	0·28	0·44
Fe_2O_3	0·38	0·48	0·48	0·44
CaO	30·25	30·41	31·03	41·91
MgO	21·28	21·26	21·05	11·75

The chemical analysis showed that grey and dark grey samples which constitute the bulk are fairly pure dolomite containing only 1·00 to 1·44%, $SiO_2+Al_2O_3+Fe_2O_3$. The lime and magnesia of the sample vary from 30·4 to 31·0% and 21·0% to 21·26% respectively. The high lime content of grey and white mixed sample indicates the presence of calcite as an impurity.

Petrographic study of the different coloured dolomite showed that all the samples are typical dolomites. The presence of calcite was very difficult to detect under the microscope. Quartz was not present while a minute quantity of talc was observed which contributes up to 0·62% to 0·87% silica in some samples.

Differential thermal analysis of the grey and dark grey samples diluted with three times the weight of calcined alumina (Fig. 1) showed that it is a typical dolomite giving endothermic peaks at 745°C–750°C and 865°C whereas the thermogram of white rhombohedral crystal carefully separated from whitish veins of the dolomite, showed one endothermic peak at 870°C–875°C which is typical of calcite. The presence of calcite was thus confirmed by the D.T.A.

The physical appearance of the calcined lumps is shown in Fig. 2. The top row shows dolomite calcined at 1 600°C and the bottom one shows dolomite calcined at 1 700°C. The fired sample showed minute cracks with large volume shrinkages. No dusting or sticking was observed after calcination at 1 620°C but sample calcined at 1 700°C showed slight sticking tendency. Some of the ½ in lump samples showed small amount of dusting. To get the ½ in lumps a portion of the big lumps was crushed. At the time of crushing, fracture took place along the zone where the siliceous material, talc was present, exposing siliceous portion which dusted after calcination. But when the siliceous pockets were inside the big lump, no dusting was observed visually.

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The porosity and bulk density of the calcined samples are shown in Table II. It may be noted that the porosity and bulk density of calcined product depends on the size of the specimen and the temperature of calcination. 4 in lump sample calcined at 1 700°C for 3 hours showed bulk density varying from 1·88 to 3·2 gm/cc and porosity 10% to 47%. Most of the samples have bulk density between 2·5 to 2·8 gm/cc.

TABLE II Bulk density and porosity of calcined dolomite

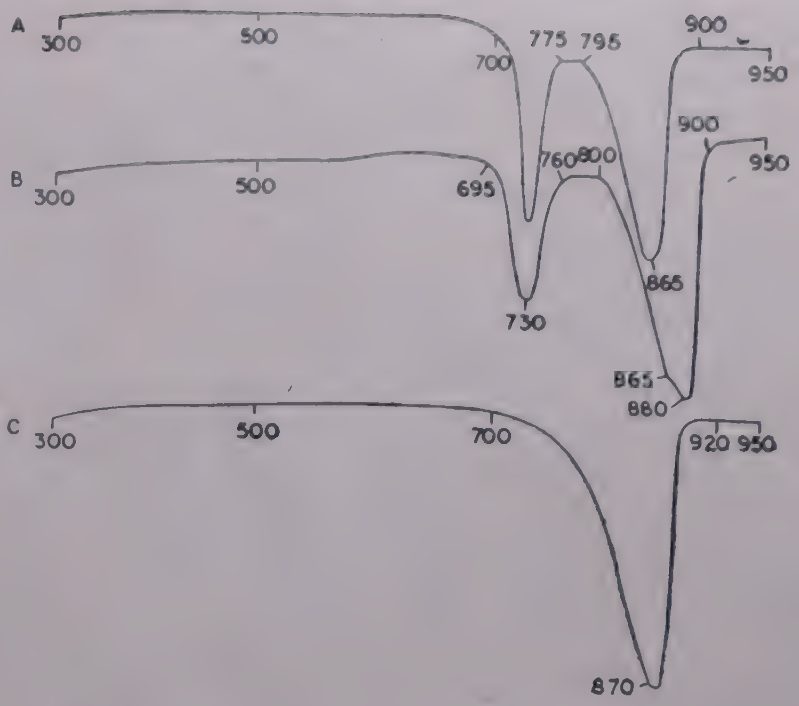
	Calcined at 1 600 C			Calcined at 1 700°C	
Size of the specimen	Bulk density gm/cc	Porosity %	Size of the specimen	Bulk density gm/cc	Porosity %
4 in	1·8	44·9	4 in	1·98	47·2
	2·34	30·0		2·49	29·7
	2·81	26·5		3·06	15·4
	2·08	36·9		2·79	22·9
	2·42	31·1		3·20	10·8
	1·91	41·1		2·49	31·34
				2·68	30·61
				2·43	32·6
				2·33	38·5
				2·79	23·4
1 to 2 in	2·13	36·3	1 to 2 in	2·66	20·7
	2·14	38·3		2·12	44·2
	2·71	20·0		2·42	25·3
	2·35	32·53		3·11	5·97
	2·77	21·05		2·70	13·48
	2·99	35·72		2·20	42·1
	2·44	32·4		2·04	40·6
	2·63	24·3			
½ to 1 in	2·0	40·0	½ to 1 in	2·11	11·7
	2·3	37·5		1·97	23·08
	1·96	44·4		2·43	18·5
	2·0	37·0		2·87	5·12
	2·10	37·1		2·71	20·37
	2·14	35·7		3·43	17·65
	2·10	37·1		2·90	18·65
	2·24	32·0			

Another set of experiments were carried out using lumps of ½ to 1 in and 1 to 2 in sizes. When fired to 1 600°C the bulk density of both sizes varied from 1·97 to 3·43 gm/cc. The fairly wide variation in the bulk density values of even one size range is due to the fact that the periphery was more sintered as compared to the core. The bulk density values of the different sizes indicate that in the case of 4″ lumps which are usually preferred for a shaft kiln charge, a temperature of 1 700°C or above would be required to get a good sinter.

Hydration tendency of the dolomite

Atmospheric hydration of the fired dolmite at room temperature showed that samples calcined at 1 600°C for 3 hours resisted hydration for 3 days whereas those calcined at 1 700°C for 3 hours resisted hydration for about 7 days. But if the core of the 4 in lump specimen, having bulk density of about 2 gm/cc or a sample containing an impurity of calcite is tested, it would hydrate after one day. Some of the calcined samples coated with boiled tar resisted hydration for one and half to two times that of an uncoated sample, similar in appearance.

Though the addition of about 2% iron oxide or millscale is known to improve the bulk density and hydration resistance, these were not tried as this investigation was concerned more with the suitability of the dolomite for sintering in shaft kilns where such additions were not practicable.

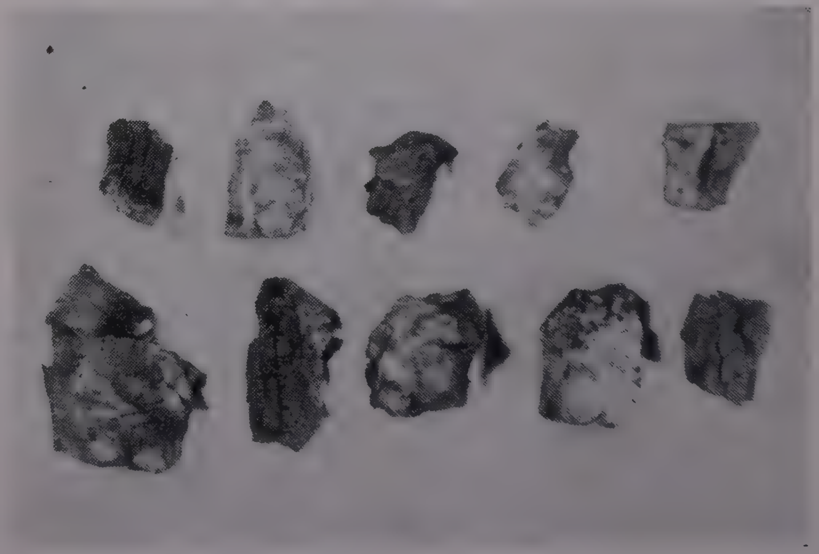


1 *Differential thermogram of dolomite samples.*

A. Typical dolomite.

B. Dolomite+Calcite sample.

C. Calcite separated from dolomite sample. (White crystal)



2 *Physical appearance of calcined dolomite.*

Top row—Samples calcined at 1 600°C.

Bottom row—Samples calcined at 1 700°C.

Trials for complete stabilisation

To study the suitability of the dolomite for complete stabilisation, about 25 parts of serpentine was added to the powdered dolomite together with 0·5 to 1% boric acid based on earlier experience with stabilisation of dolomite[2, 3]. Bricks were made and fired at 1 650°C for 3 hours. The fired material was crushed, graded and tamped with sulphite lye as a binder. A second firing at 1 600°C was given to these tamped bricks. The porosity and bulk density of the final brick was 27·3% and 2·45 gm/cc respectively. The refractoriness-under-load value was 'ta' 1 650°C and 't_e' 1 800°C. The bulk density of the final product was low and porosity high which can be brought to specified values by proper pressure and firing at a higher temperature.

Conclusions and recommendations

The dolomite was fairly pure and suitable for both semi-stabilisation and complete stabilisation. Since the dolomite is contaminated with calcite, selective mining is recommended. As the calcite occurs in isolated pockets, veins and streaks white in colour, selective mining should not be difficult. To get a uniformly dense product, the size of the charge should preferably be between 1 to 2 inches as is normally the case for calcination in a rotary kiln. However, if the dolomite is to be calcined in a gas fired shaft kiln and design considerations preclude the use of such small size, the alternative size would be from 1 to 4 in excluding all fines below ½ in and lumps above 4 in It is, however, necessary to

Acknowledgements

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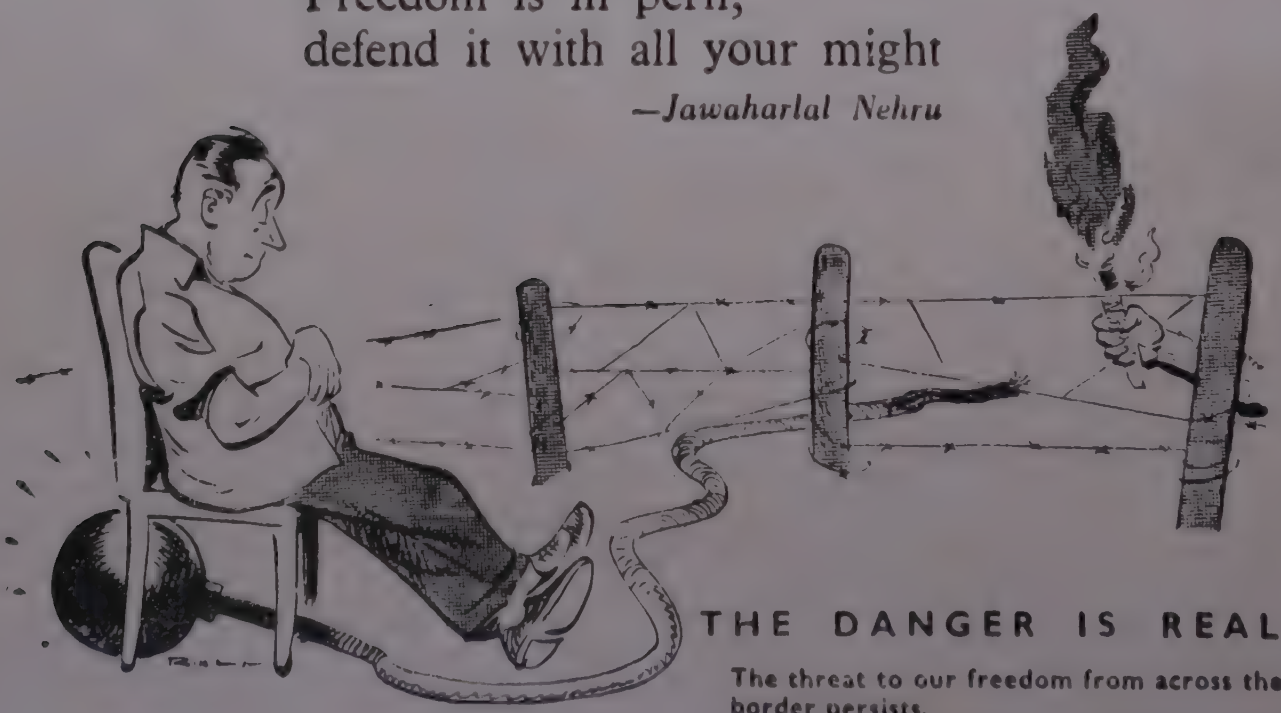

Freedom is in peril,
defend it with all your might
—*Jawaharlal Nehru*

THE DANGER IS REAL

The threat to our freedom from across the border persists.

Do not slacken your vigilance. Help strengthen defence by discipline and resolute work.

MAKE YOUR EFFORT REAL TOO

Some experiences and prospects with low-grade iron ores of Rajasthan

C. F. Rekar
J. Zakrajsek

IT can be presumed that at the end of this millenary the number of India's inhabitants will reach 600 millions and they will need at least 100 million tons of crude steel yearly. This quantity of steel will correspond to about 80–90 million tons of pig iron.

India has one of the richest and best deposits of iron ore in the world. There are probably much larger deposits than what is stated today. But even the present figure of 21 000 million tons is sufficient to provide for big future production for a long time to come. The situation regarding the coking coal however is less favourable. The total deposits of coal amounting to 60 000 million tons are mostly limited to the geological Gondwana system in the States of Bihar, Madhya Pradesh, Orissa, Maharashtra and Andhra Pradesh. Only a quarter of these coals is fit for the production of metallurgical coke, its quality not even being the best.

As big concentrations of iron ore and coal occur in the States of Bihar, Orissa, and Madhya Pradesh, gigantic ironworks with big tonnage productions have been developed and are developing in these States which give the best conditions for an economical production. It is expected that the development will demand at least 80% of the realised pig iron production and will be produced at the big plants in the above States and areas. The products of these big iron and steelworks will have to be transported by railway and also by ship to the remote consumers.

The experiences of the last 25 years show that small works also can be profitable and economically set up. These small ironworks and foundries should be uniformly located all over the country if we want to achieve conditions for a general industrial evolution. It is evident that India needs a large number of such ironworks to be built. They should be distributed on its huge territory, measuring about 3 300 000 km^2 on which 400 million of inhabitants will soon live.

These small ironworks will also be able to exploit the numerous iron ore deposits which are insignificant for a big production and are probably distributed in the other areas and States of India. For such ironworks the question of limestone is not a problem as small limestone deposits are also abundant. For such factories only the questions of industrial water and fuel are critical.

India has big deposits of lignites and other non-coking coals. The deposits of lignite are estimated at 2 000 million tons. The biggest deposits pertain to the Neyveli lignite in Madras. Coals and small size coke cannot be used by big ironworks which will in the near future represent the main reductant for these ironworks.

The Government of India has granted licences for the erection of five small ironworks with a capacity of 100 000 tons each, for the production of foundry pig iron which is so much needed for the high quality foundry and machine production. This includes a licence for a 100 000 tons pig iron production in Rajasthan. Rajasthan has a big number of small iron ore deposits. Amongst them the most important are in the Udaipur and Jaipur area. The bore drillings and samples show that about 9–10 million tons of ore can be estimated with an average iron content of about 47–50% Fe 40 miles south of Udaipur on the Natharakipal hills iron ore deposits in the Daralmata and Amsiwali area.

The average chemical analysis of an ore sample is given below:

	%
Fe	48·39
Fe_2O_3	68·71
FeO	0·57
SiO_2	27·94
Al_2O_3	1·00
TiO_2	0·005
CaO	0·16
MgO	0·32
P_2O_5	0·05
P	0·0218
S	0·05
Loss on ign.	0·49
Cu, As, Sb	traces

Prospecting and drilling are still in progress and the information about the quality and quantity of these ores is not yet definite. But the available data show that this is a very pure hematite with a low P content in general.

The ore consists mostly of a specular hematite and in minor quantities of magnetite. The iron minerals are intergrown with quartzite. The hematite grains are as small as 20 to 70 microns but their aggregates have a size from 0·2 to 3 mm. The size of magnetite grains is up to 0·35 mm. Dimensions of the crystals are from 0·25 to 0·55 mm or even more.

A low P content pig iron makes it possible today to sell it at higher prices than a normal foundry pig iron. The prices increase when the P content in the pig iron is lowered from 0·10 to 0·06% P. If such a low P pig iron can be produced, probably a selective mining will be necessary. The Amsiwali deposit seems to have iron ore with a lower P content and less variations

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in it. Recently analysed samples phosphorus contents seem to be in inverse relations.

To be able to reduce the coke and energy consumption as much as possible, such ores have to be concentrated. The investigations at the Metallurgical Institute, Ljubljana, about the possibilities of beneficiation and utilisation of such ores for a quality pig iron production on a small scale are presented.

The ore minerals are relatively finely intergrown with the gangue minerals. The attempts to upgrade them with gravity (jigs) and magnetic methods were therefore not successful. In a high intensity dry magnetic separator only an insignificant concentration was achieved when the ore having 50% Fe was ground to −3 mm. Even when the ore was ground to −1 mm the iron concentrate assayed only 55% Fe when the recovery was 91·9%. A maximum concentration of 58% Fe with a yield of 80% can be achieved by a dry high intensity magnetic separation. The results obtained with the gravity separation in a jig were not better. The concentrate never assayed over 53% Fe, because the liberation of iron minerals from the gangue was incomplete.

The flotation as a method of concentrating the iron minerals has been considered only a decade ago as expensive. But in the last ten years a considerable progress concerning the reagent consumption and good results as well in the cases where the hematite is accompanied by quartzite as gangue minerals have been achieved. Especially in the US and the USSR the flotation of this type of ore is performed industrially.

In this case the flotation is performed with different fatty acids or petroleum sulphonates.

The oleic acid and tall oil—a by-product of the paper pulp industry—are the fatty acids generally used. Whenever possible the use of tall oil is preferable because of its low price. The use of such acids mixed with various proportions of neutral oil such as fuel oil, with a water or oil soluble emulsifier, allows a considerable saving in reagent costs. These emulsions enable in most cases to float the ores without previous desliming.

The direct flotation method was adopted for concentrating the siliceous Nathara-ki-pal iron ores. Iron minerals were removed as froth product and no difficulties were encountered. The results agree in many respects with the literature statements.

The ore was ground to 300, 200 and 100 microns. When the ore is ground to 300 microns the recovery is essentially the same as when it is ground finer, only the concentrate has a 3% lower Fe content although the conditions are the same. Also if the ore is ground down to 200 or 100 microns the results are no better except that a slightly higher quantity of reagents is necessary.

A 15 minutes conditioning time is sufficient to prepare the ore for the flotation step. A shorter conditioning time diminishes the recovery and quality of the concentrate.

The pH can be changed in a wide range in the acid circuit but was mostly held near 6. In the alkaline circuit the recovery and the quality of the concentrate are poor. For the pH regulation, the sulphuric acid was used.

During conditioning, the pulp density was held between 60 and 70% solid and can be held during the flotation step as high as 45%. Lower densities do not improve the results.

When the ore was not deslimed the rate of tall oil or of oleic acid to the fuel was 1 : 2. The lowest possible emulsifying agent (alkyl-aryl-sulphonate) quantity was not studied. 5% of oil quantity was added in most

When crude tall oil was used the agent was lower. When the ore was deslimed before flotation a 1 : 1 ratio gave satisfactory results.

Sulphuric acid is the best gangue depressant. Sodium silico-fluoride, calgon (sodium-hexa-meta-phosphate) and water glass alone are less effective ; the concentrates assay 1 to 2 per cent less iron, the recovery being the same. Water glass used in quantities more than 200 g/t in conditioning depresses the iron minerals. The result was a lower recovery and concentrate assay. Sulphuric acid gave a slight depressing effect on phosphorus minerals.

During grinding an insignificant portion of a slime is formed. When the ore is deslimed the quantity of reagents can be lowered but the quality and the recovery of the concentrate do not change.

Some typical tests with an average Amsiwali ore sample are as follows :

In the first series of tests the ore was floated with tall oil. Because at present the tall oil is not produced in India some series were tested with oleic acid produced by the Calcutta Chemical Corporation.

Collector tall oil

(a) Grinding : 100 per cent −200 microns (59 per cent −70 microns) ; ground ore not deslimed.

Reagents g/t	Flotation	Cleaning	Recleaning
Sulphuric acid	500	1 000	
Tall oil	1 500		
Fuel oil	3 000		
Emulsifying agent	225		
Conditioning time	15 min		
Flotation time	2·5 min	3 min	3 min

The results are given in Table I.

TABLE I Test No 1

Products	Weight %	Assay % Fe	Distribution % Fe
Fe concentrate	65·8	68·25	92·4
Recleaner tails	3·4	42·07	2·9
Cleaner tails	6·0	18·94	2·4
Flotation tails	24·8	4·48	2·3
Head (calcul.)	100·0	48·50	100·0

From the above table it is evident that satisfactory concentrates can be obtained without recleaning.

In order to lower the reagent consumption the ore was deslimed prior to flotation. To compare the effect of desliming the test conditions and results are specified below :

Grinding : 100 per cent −200 microns and 100 per cent −100 microns (66 per cent −70 microns).

Desliming : in a laboratory hydrocyclone 30 mm.

Slimes are substantially 100 per cent under 15 μ.

Reagent g/t	flotation	cleaning	recleaning
Sulphuric acid	500	1 000	
Tall oil	900		
Fuel oil	1 800		
Emulsifying agent	135		
Conditioning time	15 minutes		
Flotation time	3 min	4 min	3 min

The results are given in Tables II and III

TABLE II—Test No. 2

Products	Weight %	Assay % Fe	Distribution % Fe	Remarks
Fe concentrate	66·0	68·40	94·9	grinding 200 microns
Recleaner tails	2·6	17·13	0·9	
Cleaner tails	6·8	5·70	0·8	
Flotation tails	22·4	3·27	1·5	
Slimes	2·2	40·80	1·9	
Head (calcul.)	100	47·6	100	

TABLE III—Test No. 3

Products	Weight %	Assay % Fe	Distribution % Fe	Remarks
Fe concentrate	46·0	68·27	93·1	Grinding 100 microns
Recleaner tails	3·1	26·30	1·7	
Cleaner tails	6·5	6·99	1·1	
Flotation tails	21·4	3·01	1·3	
Slimes	3·0	45·22	2·8	
Head (calcul.)	100	48·43	100	

Only 1·9 and 2·8 per cent iron respectively is lost in slimes but the reagent consumption is considerably lower when the ore is deslimed prior the flotation. From the standpoint of the flotation technology grinding to microns is satisfactory.

Collector oleic acid

To compare the effectiveness of oleic acid against the tall oil some tests were performed. The principal goal of these tests was to hold the reagent consumption as low as possible. Deslimed and non-deslimed ore were floated.

The most successful results are given in the following tables :

Grinding : 100 per cent under 200 microns

Reagent g/t	Flotation	Cleaning
Sulphuric acid	1 000	500
Oleic acid	480	
Fuel oil	960	
Emulsifying agent	72	
Water glass	200	
Conditioning time	15 minutes	
Flotation time	3 ,,	1·5 minutes

TABLE IV—Test No. 4

Products	Weight %	Assay % Fe	Distribution % Fe	Remarks
Fe concentrate	65·1	66·9	92·7	not deslimed
Cleaner tails	8·5	21·33	3·9	
Flotation tails	26·4	5·86	3·4	
Head (calcul.)	100	46·25	100	

TABLE V Test No. 5

Products	Weight %	Assay % Fe	Distribution % Fe	Remarks
Fe concentrate	68·6	66·38	93·2	Deslimed
Cleaner tails	8·9	19·25	3·5	
Flotation tails	20·3	3·33	1·4	
Slimes	2·2	40·80	1·9	
Head (calcul.)	100		100	

Recoveries are lower than above. It seems that the quantity of reagents is just a little under the limit. This is the reason why the recovery of the non-deslimed ore is lower than the deslimed ore. Following is the complete analysis of the concentrate obtained.

Fe total	66·38%
Fe_2O_3	93·46%
FeO	1·41%
SiO_2	3·80%
Al_2O_3	0·51%
CaO	0·14%
MgO	0·05%
Mn	0·11%
P_2O_5	0·045% (P=0·02)
S	0·05%
Loss on ign.	0·18%
Cu, Cr, Ti, As	0·01%

The screen analysis of the concentrates of the above tests is given in Table VI.

TABLE VI Screen analysis of the concentrates

Screen opening microns	200 microns grind		100 microns grind	
	deslimed	not desl.	deslimed	not desl.
160	2·5	3·4		
100	17·3	17·5		
71	27·5	25·7	18·8	19·4
60	13·7	10·7	21·9	18·6
minus 60	39·0	42·7	60·2	62·0

When the reagent quantity is increased the recovery rises. Results obtained are shown in Table VII.

Grinding : 100 per cent under 200 microns, ore not deslimed. Reagents g/t :

	flotation	cleaning
Sulphuric acid	1 000	1 000
Oleic acid	960	
Fuel oil	1 920	
Emulsifying agent	144	
Water glass	200	
Conditioning time	15 min	
Flotation time	1·5 ,,	1·5 min

TABLE VII Test No. 6

Products	Weight %	Assay % Fe	Distribution % Fe
Fe concentrate	71·5	67·15	96·5
Cleaner tails	8·1	16·41	2·7
Flotation tails	20·4	1·90	0·8
Head (calcul.)	100	49·71	100

The reagents were given in excess, therefore the flotation was quick, the recovery and quality of the concentrate better than in the last two tests.

The production costs of such an iron ore concentrate may be in India of special interest in contrast with the very low costs for high-grade ores produced in the big ore mines in the eastern areas. The mining costs in such small mines are higher. Calculated for the Natharaki-pal mines it has been arrived at Rs 9·9–9·5 per ton (including royalties, and other expenses). Taking into account Rs 5·5 for transport of 1 ton of raw ore on to the ironworks stockyard, the cost would come to Rs 14–15 per ton. Thus one ton of iron in the raw ore costs about Rs 28–30 when the beneficiation plant is located at the ironworks itself (because of the water supply, etc).

The beneficiation costs with interests, etc. for each ton of concentrate would be about Rs 9–10. One ton of 66% concentrate costs Rs 37–40 and one ton of iron in a 66% concentrate Rs 58. For one ton of pig iron which contains 94% Fe this will cost about Rs 52–54.

It is supposed that these costs per ton of iron in the ore are much higher than those of a raw high grade ore at the big Indian blast furnaces. It may be therefore economical to concentrate such low grade ores only if they are very pure and if such concentrates can be used as raw materials for a high quality pig iron or special iron production. Having 67·68% Fe they could be reduced to sponge iron pellets or briquettes of importance for special steel productions.

The screen analysis of the ore ground to 200 and 100 microns shows that such concentrates cannot be transformed to sinter economically, but may be pelletized. The screen analysis of the ores ground to 100 microns is more convenient for pelletizing, but a large number of pelletizing tests prove that ore concentrates ground to 200 microns also give good pellets. For these pellets some additions of bonding (like bentonite, $CaCl_2$, lime, cemen, tetc.) to an amount of 1–2% are necessary. These pellets can be hardened at 1 100–1 200°C on a sintering grate till to a reduction degree of 40–50% or in a rotary kiln to sponge iron. On the grate it is rather difficult to obtain uniformly pre-reduced pellets. The pre-reduction degree varies too much between 40 and 60% so as to have later a uniform reduction process in the electric furnaces. As burden in the low shaft furnaces such differences are also too much. In a rotary kiln it is easier to obtain the reduction or pre-reduction extent to a good uniformity. But to reduce the pellets and ores till to metallic iron there will be rather big variations regarding the carbonization of the iron or its pellets. This could become disagreeable for their use as pure steel scrap for

The question of partly or pellets has become of special interest not only for pig iron production in electric furnaces but also in hot blast furnaces. It may be attractive to pelletize a mixture of fine ores and the necessary reductant and to harden and reduce them in the kiln in only one step. Large scale trials are in progress in Europe and North America to achieve this one step pelletizing and reduction. The results are promising but not yet proved successful on a very large scale industrial plant. It can be expected that during the next two or three years such difficulties may be solved. The two- or one-step pre-reduction or a complete reduction of pellets to sponge iron is of special interest for countries which have no coking coal but where semi-coke from lignite is available. Such semi-coke breeze can be used in sintering or in rotary kilns for the iron works saving in this way the metallurgical nut coke which generally is used for production of pig iron in electric pig iron furnaces and low shaft furnaces. Rajasthan has in Palana some lignite deposits which could be used to a limited extent because of their high sulphur content.

Conclusions

The paper shows the possibilities of using low-grade but chemically pure iron ores belonging to the rather small iron deposits of Rajasthan. Although the beneficiation and preparation of the raw materials is expensive and such a plant has to be considered for very small output, the production would be profitable when quality pig-iron and products are produced. This may pave the way to erect more small ironworks as a basis for the future industrial development of large Indian areas.

Notes and news

HOME NEWS

More capacity for engineering units

The union Government has decided to license larger capacities than the Third Plan target for a range of engineering and metallurgical industries including steel castings, steel forgings, etc. in order to avoid distortions in industrial production programmes during the Fourth Plan.

In the case of steel castings it has been decided to license a total capacity of three lakh tonnes against the Plan target of two lakh tonnes per annum. At present there are 17 well established units for steel castings with an installed capacity of 58 840 tonnes per annum and a production level of 48 000 tonnes. Twelve new units are expected to go into production during 1964–65 with an anticipated level of output of 65 000 tonnes by the end of this year.

As regards steel forgings, it has been decided to plan and license an overall capacity of 2·16 lakh tonnes per annum by 1965–66. At present there are 39 units with a capacity of 56 000 tonnes and a production of 54 000 tonnes per annum. In the case of cast iron castings, the total capacity planned for licensing is 9·41 lakh tonnes per annum against a target of eight lakh tonnes. At present there are 16 units manufacturing cast iron pipes, including spun-pipes with an installed capacity of 2·69 lakh tonnes. The production of cast iron pipes in 1963 was 202 013 tonnes, the short fall being due to shortage of pig iron. It is expected that an additional capacity of 30 000 tonnes per annum would be reached by 1964.

Economics Times, 1.4.1964.

Punjab Government to set up a pig iron plant

The Punjab Government have decided to set up in the public sector a pig iron plant with a capacity to turn out one lakh tons of pig iron annually. The project is estimated to cost Rs two and a half to three crores. The location and the time to start work on the project will be decided in consultation with the experts. The raw material requirements of the plant will be met from Mahendragarh district of Punjab where iron ore deposits estimated at about three million tons have been discovered.

The Hindu, 9.2.1963.

Pig iron plant for Andhra Pradesh

The Andra Pradesh Industrial Development Corporation will set up a Rs 7 crores pig iron plant in Khanmam district with an annual capacity of one lakh tons. A licence has been granted to the Corporation by Government of India.

Hindusthan Standard, 24.1.1963.

One more pig iron unit for Goa

The Union Government is considering a proposal to set up a 100 000 ton pig iron and a 1·5 million ton pelletisation plant in Goa, in addition to the two such plants already approved for the State.

Financial Express, 4.2.64.

Fourth Plan steel target

The Steering Group on steel has recommended the production target of 17 million tonnes of steel ingots, 4 million tonnes of pig iron and one million tonnes of alloy and special steels to be achievhd by the end of the Fourth Plan. The Steering Group has stated that the Fourth Plan production targets should be achieved through considerable expansion of the existing plants in the public and private sectors and by establishing four new steel plants in the public sector in addition to Bokaro and the proposed plant in South India based on Neyveli lignite.

Hindusthan Standard, 6.4.1964.

Sale of iron and steel by Hindustan Steel in 1963-64

The three plants of Hindustan Steel sold iron and steel worth Rs 180 crores in 1963-64, Rs 50 crores higher than the previous year. The combined output of the three plants was 99·4 per cent of the rated capacity in blast furnace hot metal and 97 per cent in ingot steel, while saleable steel touched 94 per cent of rated capacity, Bhilai accounted for 4·5 lakh tonnes of pig iron, Durgapur 4 lakhs tonnes and Rourkela 69 000 tonnes.

Financial Express, 8.4.1964.

Soviet aid for Bokaro Plant

Mr C. Subramaniam, Union Minister for Steel, Mines and Heavy Engineering has said that the Bokaro Steel Plant would be built with Soviet assistance.

Hindustan Times, 15.4. 1964.

Steel and zinc plant at Visakhapatnam

A 2·5 million ton steel plant costing Rs 300 crores would be located at Visakhapatnam during the Fourth Plan. Visakhapatnam would also have a zinc smelter plant costing about Rs. 10 crores.

Economic Times, 22.4.1964.

Gypsum deposits found in Garo Hills

The Directorate of Geology and Mining, Assam, is reported to have located a gypsum deposit at Gangrapara near Mahenderganj in the Garo Hills. The State Government is conducting prospecting operations in the area.

Statesman, 12.4.64.

Coal reserves in India's Eastern belt

The reserves of class I coal (selected A and seclected B) in the Jharia, Raniganj and East Bokaro coal fields having an ash content up to 17 per cent has been estimated at 1 103·51 million metric tons, according to an assessment of an expert committee. Of the total reserves, Jharia accounts for 661·79 metric tons, Raniganj for

418 71 million metric million metric tons.

Hindusthan Standard, 13.4.1964.

Manganese ore export down

India's efforts to boost manganese ore export have not been successful. Both in terms of quality and value, exports have declined sharply since 1957–58. As against 17 lakh tonnes of ore valued at Rs 30 crores exported in 1957–58, shipments in 1963-64 are estimated at not more than 10 lakh tonnes worth Rs 8 crores. This is attributed to the emergence of new sources of supply in Brazil and French Africa and of keen competition from Russia, which has, of late, been supplying high grade ore to UK, Germany, Italy and France.

Hindustan Times. 14.4.1964.

Production of plutonium at Trombay plant

The Atomic Energy Establishment at Trombay has announced the completion of its project 'Phoenix', a plant to extract plutonium from waste fuel elements—the 'ash' from the three atomic reactors at Trombay. The plant was designed and built at a cost of Rs 3·6 crores entirely by Indian scientists and technicians and without any foreign collaboration. The plant was designed to extract plutonium from 30 tons of uranium annually,

Hindustan Times, 16.4.1964.

OVERSEAS DIARY

Steel output expanding in Britain

Output from Britain's steel mills is rising according to estimates made by a number of leading UK companies. One authoritative estimate was that production overall is now running at an annual rate of 27 million tons, compared with the recently revised target of 25·5 million tons for 1964 as a whole.

Financial Times 10.3.1964

German steel orders at record level

A burst of demand from German consumers caused new orders booked by the West German steel industry to reach a record level of 2·17 million tons of rolled products during February, compared with a monthly average of 1·76 million tons in the last quarter of 1963. Demand for steel has improved primarily because of continuing boom in the motor industry. Stocks also seem to have been run down to the point where restocking has become necessary. The total crude steel output of the first two months of this year in West Germany totalled 5·9 million tons. If this rate is maintained the production record of 34·1 million tons set in 1960 would be improved on or at any rate matched.

Financial Times, 10.3.1964.

New steel plant in Belgium

A new cold rolling strip and sheet mill is to be erected in the Liege area by a joint subsidiary of the Pittsburgh Steel Company and the Armco Steel Corporation. The construction work, which is in the hands of the Belgo-American Engineering group 'Evence Coppee-Rust', is to begin very shortly and is scheduled for completion in time for production to start before the end of next year.

Financial Times 18.3.1964.

A new and fully integrated steel plant is being built at Taranto, South Italy, by Italsider which has the largest output of any steel company in Europe. This steel centre has been designed to achieve an ultimate capacity of 6 million tons of steel. By next year it will be producing 2·2 million tons of steel, 1·8 million tons of flat hot rolled section, 200 000 tons of longitudinally welded pipes, 20 000 tons of scrolled rolled pipes, as well as 2 million tons of cast iron.

Financial Times 7.2.1964

Russian iron ore industry

One of the outstanding features of the iron ore industry of the Soviet Union is the rapid development of opencut working of ore deposits. The contribution of ores obtained in this way in 1962 was 62% of the total amount won compared with 45% at the start of the current Seven-Year Plan in 1958. Especially startling results in this sphere have been achieved by miners in the Krivorozh area in the Ukraine ; a few years ago the volume of open-cut ore did not exceed 17% of total output, but in 1962 about half of the ore won in this district came from open-cut mines.

Open-cut working has led to the exploitation of ore sources with low iron contents. In 1962, the open-cut method produced 116 million tons of raw ores, from which more than 70 million tons of iron ores and concentrates were subsequently processed. New techniques are finding increasing use in iron ore mines. These include more productive drilling equipment.

The 1962 plan for the iron ore industry has been fulfilled. More than 180 million tons of raw ore were won. Beneficiated iron ore amounted to 120 million tons, which was 8–9% more than in 1961 and 56 million tons more than was produced in the U.S.A. according to the Russians. The cost of raw ore was cut by 5% a ton over 1961 costs.

With the expansion in the open-cast method of working, the weight of ore obtained by the under-ground method has dropped from 51·5% of the total output in 1951 to 36% in 1962. The absolute weight of underground mined ores has grown by 10·3% since 1958, and in 1962 it reached 65 million tons. In 1962 the average Fe content of Russian ore was 55·1%, compared with 54·6% in 1961. The increase was due chiefly to the increase in proportion of beneficiated ores.

Russian metallurgists place heavy demands on ores for the smelting process. In 1962 more concentrates and fines were caked by the sintering method : 83·28 million tons of agglomerate (sinter) were produced compared with 74·2 million tons in 1961. Enrichment plants also produced 1·2 million tons of open-hearth sinter. But the demands for enrichment exceed production capacity and there is a great need for new sintering machines. In 1962 the plan for introducing new capacity was only a third completed. This is hindering the supply of metallurgical plants with blast and open-hearth sinter.

Iron and Steel, 37 (2), 1964.

Continuously cast vacuum degassed steel

Research at Bisra into the continuous degassing molten steel has now culminated in a practical application at the Low Moor Alloy Steel Works at Bradford, linking up continuous degassing and continuous casting. A heat of 18/8 austenitic stainless steel was degassed in the

Bisra plant erected at Low Moor, part of which was continuously cast into a 5½ in diameter bar. This is believed to be the first time in the world that vacuum degassed steel has been continuously cast.

Metallurgia 68 (410), 1963

£3 000 000 Tunisian order for British steelmaking plant

A British firm is to supply the sinter plant and blast furnace for Tunisia's first major iron and steel works at Menzel Bourguiba. The £3 000 000 contract was awarded to Ashmore, Benson, Pease and Co., a member of the Davy-Ashmore group. Work is due for completion in 2½ years.

Journal of Iron and Steel Engineering, Nov. 1963

Seventh International Mineral Processing Congress

The Seventh International Mineral Processing Congress will be held in New York City from 20th to 24th September, 1964. The programme will include sessions on comminution, gravity and dense-media separation, magnetic and electrical separation (with emphasis on significant new developments in high-intensity wet magnetic separation), surface chemistry in mineral processing, flotation kinetics, chemistry of flotation, flotation practice, chemical processing, automation and control. There will also be a special symposium on autogenous grinding.

The Indian representative on this International Scientific Committee is Mr P.I.A. Narayanan, Officer-in-Charge (Ore-Dressing), National Metallurgical Laboratory, Jamshedpur.

Recent developments

The FOS steelmaking process

More details are now available for Bisra's FOS method of steelmaking which was reported earlier. The basis of the FOS technique has been established on a half-ton scale in Bisra's Sheffield melting shop and confirmed by trials on a five-ton scale in a local works. For maximum heat transfer, a cylindrical vessel is preferred and to permit rapid basket charging the roof is movable. The roof carried a single 'Toroidal' burner (developed by the Shell International Petroleum Company) and waste gas removal ducts. The absence of elaborate electrode movement mechanisms and of supply transformers and switchgear makes the capital cost very much less than that of an arc furnace. The likely need to fit arc furnaces with voltage fluctuation compensation equipment will add a further cost advantage to the process.

In operation, the charge normally consists of scrap steel, lime and carbon. To ensure a boil during subsequent refining, it is basket-charged, the roof is replaced and the burner ignited. As the metal melts away, the burner is lowered till a molten pool forms on the furnace hearth. The hot gases pass through and heat the surrounding scrap and the burner is withdrawn gradually to extend the molten pool and melt the remaining scrap. At this stage the bath is sampled and analysed and the fuel and oxygen rates adjusted to remove carbon and raise metal temperature so that correct composition and tapping temperature are achieved simultaneously. The heat is then blocked, the necessary finishings added, and the furnace tapped. Ingot yield has been 90–91% and rimming, carbon and low alloy steels have been made with good control of carbon and sulphur to within normal specifications. By choice of suitable refractories, lining life may be prolonged and cost kept to acceptable levels.

By working in this way, consumptions of about 22 gal of oil and 6 000 cft of oxygen per ton of finished steel have been achieved with charge-to-tap times of 1½ hr. Operating times of as little as 45 min have been reached on the half ton unit, where higher specific firing rates have been possible. The cost of such quantities of fuel oil and tonnage oxygen is lower than that of electric power and electrodes in arc furnace steelmaking.

A detailed estimate of the capital and operating costs has shown that with plant suitably designed for annual outputs of 70 000 tons or more the cost of ingot making will be 15s to 20s per ton less than with electric steelmaking on a similar scale. The FOS process will show to particular advantage where arc furnaces are subject to heavy maximum demand charges and where production has to cease during certain restricted hours.

The trials have demonstrated that both heavy and light scrap may be used in the process and that, as an alternative carburizing agent, pig iron up to at least 50% of the charge may be conveniently employed. The process can therefore make the best use of available supplies of raw material to achieve low cost.

In spite of the relatively large volumes of oxygen used, the process is characterized by the absence of red fume. Sampling in the exhaust stack has shown dust concentrations over whole heats of 0·01–0·02 cft, which are well below the statutory limits. There is thus no need for expensive dust cleaning facilities.

The FOS process offers an economic steelmaking method that permits steelworks, with or without a blast furnace, to replace open-hearth furnaces with an oxygen process rather than with electric arc furnaces. Indeed it makes it possible for LD shops to avoid damaging converter linings during charging of scrap and to melt the latter in units properly designed for the purpose.

Iron and Steel, 37 (1), 1964

Vacuum degassing and induction melting for ultra clean alloys

In western Pennsylvania, a unique vacuum melting unit is being built. Called the 'Therm-I-Vac' process by Latrobe Steel Co., it is said to be capable of making super pure metals and alloys in quantities never attained. Operations begin with the air melting of virgin raw materials and vacuum melted revert scrap in an electric furnace. When the heat—it can weigh up to 60 000 lb—is ready, the hot metal is poured into a ladle. Immediately, a crane carries it to the vacuum unit, where it is positioned over the charging post.

Vacuum locks connect the ladle to the unit. When the desired vacuum is reached, the hot metal pours directly into the vacuum induction crucible. As the hot metal heats the vacuum, it explodes into thousands of tiny droplets as gases rush from the steel to be pulled out by steam ejector pumps. Stream width is controlled by a sleeve, which keeps the splash to a predetermined pattern.

When charging is finished, the melter starts the induction furnace. As pumps quickly bring the vacuum down to a range of 1 to 5 microns, more oxygen, hydrogen and other gases boil out of the melt. A vigorous carbon boil refines and further degasses the bath. Meanwhile, magnetic stirring aids in removing the last traces of gas and creates a uniform composition by constantly exposing fresh metal to the controlled vacuum.

Next any necessary alloys are added through the charging post. Technicians periodically extract samples of the melt by a remote control mechanism operated from within the bulk charges and send them by pneumatic tube, to the chemical laboratory. As soon as the heat reaches the desired composition, vacuum casting can be started.

Before hot charging is begun, ingot moulds are put in position under vacuum. When the heat is ready, the poures move the mould under the tundishes from which the molten metal streams. As soon as the heat is cast, the vacuum is broken and the ingot mould is removed from tunnel for stripping.

The 'Therm-I-Vac' concept is a result of the joint efforts of Latrobe Steel Co., F. J. Stokes Corporation and Inductotherm Corporation.

Metal Progress, 85 (1), 1964.

Ultrasonic cleaning of steel strip

Steel strip is fed at a maximum speed of 100 ft/min into the ultrasonic strip-cleaning machine recently built and installed for the Carpenter Steel Corporation. Designed to handle strip thicknesses from 0·083 to 0·220 m and widths from 4 in to 15½ in, the strip enters the machine and is subjected to the following process cycles : entrance and squeeze, soak wash, ultrasonic wash, drain and squeeze, spray rinse, drain and blow-off.

Tank sections of the assembly are provided with overflow dams, drain sumps, large sludge-cleanout doors, suction screen access doors, and perforated flush-out pipes. The housing portion of the assembly is provided with vapour-tight access doors above each processing stage. The soak wash and ultrasonic wash tanks are suspended in the housing by structural members. This latter tank utilises the 'lip seal' method for containing cleaning solution at proper level. The wash pump draws cleaning solution over heating coils and discharges into the soak and ultrasonic wash tanks. An overflow connection in this latter tank returns the solution to the main reservoir thereby maintaining proper level in the processing tank.

A flow regulating valve and pressure gauge are provided in the pump discharge line. This pump draws rinse solution over the heating coils and discharges into spray manifolds mounted above and below the pass line. Each spray manifold is provided with individual shut-off valves and high impact 'spraying systems', veejet type nozzles, threaded into manifolds to thoroughly cover the strip. The individual manifolds may be removed from the side of the machine for nozzle service. This allows the balance of the system to operate while one manifold is being serviced. Two flow control valves are provided above and below the pass line with pressure gauges to adjust spray pressure.

The last manifolds above and below the pass line use tap water. This water is directed through a 'Taco' shell and tube-type heat exchanger at a rate of approximately 12 gal/min. An 'American' indicating-type direct acting steam regulator with stainless steel bulb is provided to regulate discharge water temperature at approximately 82°C.

Face rolls are provided throughout the machine. The lower rolls utilise flange type self-aligning bearings, with spring and hand wheel adjustment for proper tension. The upper and lower rolls are mounted for removal from the side of the machine.

The ultrasonic equipment is of modular design. Each transducer is driven by an individual generator matched and tuned to the transducer frequency. In a large installation the advantage is that in the event of a transducer or generator failure, the remaining units will run until maintenance permits servicing of the failure. The 24 generators, mounted in a common cabinet, are of the pulsing type and are completely transistorized with automatic turning. The generators have an average output of 250 W each, with a radio frequency of 25 kc. A total of 24 lead-zirconate-type transducers are provided 12 each above and below the pass line. Manufacturer of the ultrasonic equipment is National Ultrasonic Corpn. of Somerville, New Jersey, USA.

Metal Industry, 104 (12), 19 *March*, 1964.

Hard alloys drawn without scoring

A high melting asphalt lubricant protects refractory metals from scoring during cold forming operations such as wire drawing. It can be used with or without a superficial coating of another lubricant. Unlike conversion coats, the first coat of this lubricant spreads very thin. And in some cases, the first application lasts through several successive draws.

The lubricant was developed for the Atomic Energy Commission by General Electric's Hanford Atomic Products Operation, Richland, Wash. It tends to become a tough solid under thin-film, high-pressure conditions and keeps metallic surfaces apart. The film will not squeeze out of the die contact area until its melting point is reached.

A thin film of the asphalt clings tenaciously to metal surfaces. It can be applied by dissolving the asphalt in zylene, dipcoating the part to be formed and then allowing the solvent to evaporate thoroughly. One of the big savings claimed for this lubricant is its ease of removal. Wiping with a solvent-soaked cloth, dipping in a tank of almost any hydro-carbon or chlorinated solvent, or vapour degreasing removes the coating in just a few minutes.

Zircaloy-2, molybdenum, titanium-zirconium-boron alloy, tantalum, tungsten, columbium, vanadium and uranium have all been successfully drawn. Metals such as nickel, aluminium, pure iron, In-conel and Hastelloy have also been drawn. However, other lubricants work just as well with these metals.

Initial tests showed the cross section of zircaloy-2 could be reduced 5 to 10% per pass without scoring the part or the die. But reduction had to be aided by a spray of water. Cooling with water kept the lubricant below its melting point. As the next step, lithium stearate was applied to the asphalt surface. The stearate reduced friction. As a result, the water spray was not needed if the reduction per pass was less than 10% and the drawing speed about 10 fpm.

Iron Age, 193 (8), 1964.

New maraging steel

The International Nickel Co. Inc. has developed a new type of maraging steel for service at elevated temperatures. This newly developed steel is said to combine most of the desirable characteristics of established maraging steels—including low distortion and dimensional changes and good machinability and weldability—with a yield strength of 180 000 psi and stress—rupture life of 100 hr or more when subjected to a stress of 100 000 psi at 1 000°F.

Study showed that optimum 1 000°F properties were gained with a maraging steel containing 15% Ni, 9·0% CO, 6·0% MO, 0·7% Al, 0·7% Ti, and the balance iron.

Journal of Metals, 15(12), 1963.

Copper rod continuously cast

Details of a continuous casting and rolling process for high-quality copper rod were disclosed in a joint announcement by Western Electric Co. and Southwire Co. of Carrollton, Ga. The new process eliminates converting copper to bar form before it is reheated and rolled into rod for drawing into wire. Engineers for the two firms—who developed the process jointly—believe the new process will result in substantial savings in the production of copper rod. Briefly, the process involves a continuous, controlled flow of molten copper that pours on to a revolving wheel. The copper rim of the wheel is grooved to receive the molten metal, which is retained in the groove by a steel belt. The moving metal is water chilled into a continuous bar which leaves the wheel and passes through a rolling mill without interruption.

Southwire has used a similar process for a decade in the continuous casting and rolling of aluminium rod. Developed by Ilario Properzi of Milan, Italy, the process called for extensive metallurgical and mechanical development work before it could deal with the higher heat required to process copper.

In recent runs, the process for copper has resulted in casting and rolling rates higher than 10 tons per hour. In drawing 3/8 in rod produced by the process down to wire sizes used in house-wiring and communications circuits, Western Electric and Southwire have found that the product has a drawing performance consistent with that of other rod.

Journal of Metals, 15 (2) 1963.

Dense metal compact

In order to improve the mechanical properties of pressed and sintered parts, Battelle Memorial Institute has made a study of the high density compacting of iron powder. Metallurgists sought to determine the feasibility of achieving densities over 99% in iron and iron base compacts as compared with the current upper density limits of about 97·2%.

Battelle reports that a technique was developed for producing specimens with densities of 99·3% to 99·9% for pure iron and somewhat less for steels. These high densities were achieved by pressing and condensing specimens prior to high velocity compacting. Several electrolytic iron specimens were pressed at 20 000 to 60 000 psi, sintered 1 hr at 2 000°F in hydrogen, and then compacted explosively at about 400 ft per sec.

Journal of Metals 15 (12), 1963.

New method for coating copper with aluminium

Alloys Electronics Corporation, Massachusetts, had developed a gas plating process for coating copper and other materials with aluminium. Several unique features of the process should widen the potential application.

This plating is accomplished by the vapour-phase decomposition of a low boiling point organo-aluminium compound with plating temperatures in the vicinity of have been applied to copper. These coatings are strongly adherent, pore-free and may be anodized if desired. When anodized these coatings exhibit high dielectric strength.

The process is continuous. Interior surfaces of tubing, threaded parts and intricate shapes may be coated uniformly to a predetermined thickness. Immediate application for this new plating process may be found in the electrical and electronics fields. Application of this technique could be utilised to produce tubing or other shapes that exhibit the properties of aluminium on one surface and copper on the other with the bulk properties of copper.

Light Metal Age, December 1963.

Non-destructive test meter

The research laboratories of The British Aluminium Co. Ltd have developed an eddy current instrument for the accurate measurement of thin films on non-ferrous metals. This is an improved version of an earlier instrument which was designed at the laboratories and is available commercially. One of the main advantages of the new instrument is that it can be used for measurement of thin films, such as anodic, lacquer and paint films, on curved surfaces without excessive care in calibration checking being required to take account of the curvature. The instrument is capable of measuring anodic film thickness of from less than 2 microns to 60–65 microns (approximately 0·001–0·0024 in) with an accuracy of better than ±0·5 microns.

Metallurgia, December 1963.

Steel mould additive

The Steel Works Division of Foseco (F.S.) Ltd., announced the first ever mould additive for top teemed steel ingots. This addition produces vastly superior ingot surfaces without the necessity of coating the moulds prior to teeming. This product is non-toxic and in no way affects the metallurgical qualities of the steel. It can be applied at any time before tapping and is not dependent on the mould temperature as are many conventional dressings. Application is extremely simple and economical. A weighed quantity (2 oz/ton) is merely dropped into the untreated mould and the metal teemed directly into it.

Metallurgia, December 1963.

ERRATA

Paper entitled 'Production of High Carbon Ferro-Chrome', Vol. V, No. 4, 1963, page 19 :

the equation $F = \frac{\pi^2 R_c YDL}{N\zeta}$ should

read as $t = \frac{\pi^2 R_c Ydh}{N\zeta}$.

Statistics

PRODUCTION OF IRON AND STEEL IN INDIA

Year		Pig iron* ('000 tons)	Direct* castings ('000 tons)	Steel* alloys ('000 tons)	Steel* ingots and metals for castings ('000 tons)	Semi-* finished steel ('000 tons)	Finished* steel ('000 tons)
1955		1 756·8	126·0	12·0	1 704·0	1 456·8	1 260·0
1956		1 807·2	122·4	28·8	1 737·8	1 484·1	1 338·0
1957		1 789·2	112·8	9·6	1 714·8	1 440·0	1 346·4
1958		2 002·8	72·0	25·2	1 813·2	1 599·6	1 299·6
1959		2 958·0	44·4	21·6	2 443·6	2 220·0	1 736·4
1960		4 149·6	36·0	7·2	3 245·3	3 424 8	2 208·0
1961		4 958·4	31·0	8·4	4 071·6	1 201·2	2 845·2
1962		5 726·4	40·8	48·0	5 079·6	1 069·2	3 778·8
1963	January	570·2	...	8·8	512·8	104·0	352·3
	February	528·2	...	9·5	466·5	88·5	335·4
	March	579·7	...	10·4	539·4	105·0	395·7
	April	568·5	...	12·5	497·8	88·0	335·3
	May	574·3	...	11·2	506·7	104·7	342·2
	June	560·3	...	11·1	496·5	88·4	371·4
	July	586·9	...	10·1	506·7	97·2	...
	August	667·8	...	12·4	492·1	108·0	...
	September	547·1	...	...	482·3	89·8	...

* Figures from 1960 onwards are in thousand metric tons.

Source : Journal of Industry and Trade, Vol. XIV, No. 3, March, 1964.

PRODUCTION OF NON-FERROUS METALS IN INDIA

Year		Aluminium* (tons)	Antimony* (tons)	Copper* virgin metal (tons)	Lead* virgin metal (tons)	Non-ferrous* pipes and tubes	Gold† (oz.)
1955		7 225·2	504·0	7 281·6	2 234·4	343·2	211 494
1956		6 500·4	589·2	7 628·4	2 497·2	393·6	209 256
1957		7 784·4	531·6	7 848·0	3 174·0	394·0	179 198
1958		8 181·6	526·8	7 140·0	3 334·8	400·8	170 112
1959		17 248·8	663·6	7 641 6	3 895·2	747·8	165 312
1960		18 412·8	810·0	7 775·0	3 746·4	598·8	4 992
1961		15 908·4	620·4	8 745·0	3 663·6	970·8	4 872
1962		35 403·6	622·4	9 780·0	4 048·8	...	5 076
1963	January	4 688·2	65·0	430·0	382·0	53·6	359
	February	4 137·5	75·0	750·0	245·0	42·3	353
	March	4 515·0	75·0	900·0	493·3	32·5	375
	April	4 222·9	80·0	825·0	109·0	70·7	406
	May	4 555·2	80·0	850·0	310·0	104·2	365
	June	4 394·9	60·0	812·0	115·0	...	382
	July	4 127·0	75·0	845·0	340·0	...	357
	August	4 123·0	75·0	795·0	400·0	...	354
	September	...	85·0	740·0	247·0	...	...

* From 1960 onwards figures are in metric tons.

† Figures from 1960 onwards are in kgs.

Source : Journal of Industry and Trade, Vol. XIV, No. 3, March, 1964.

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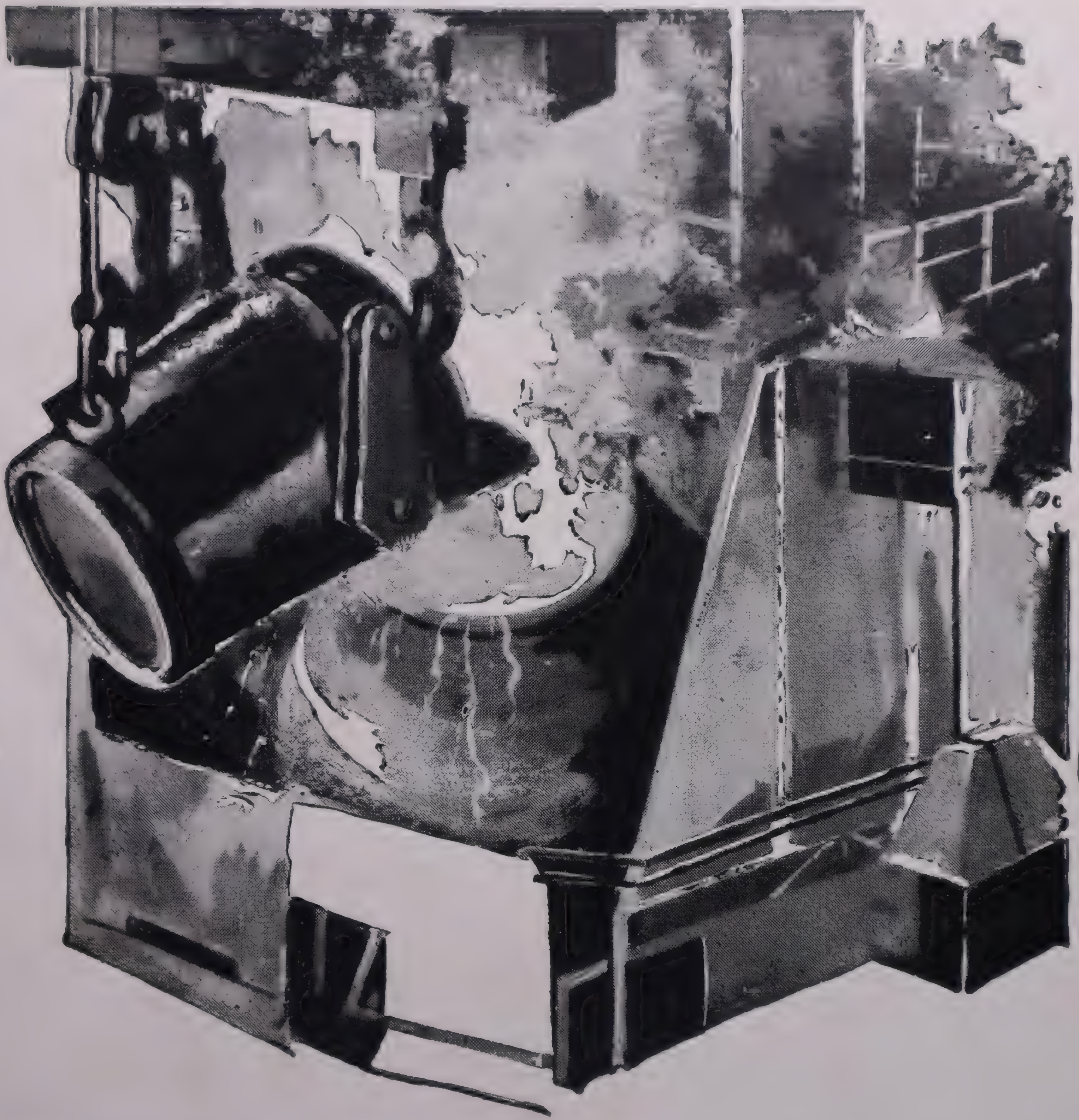

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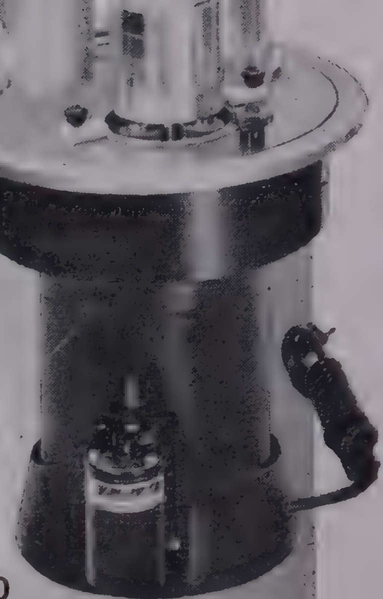

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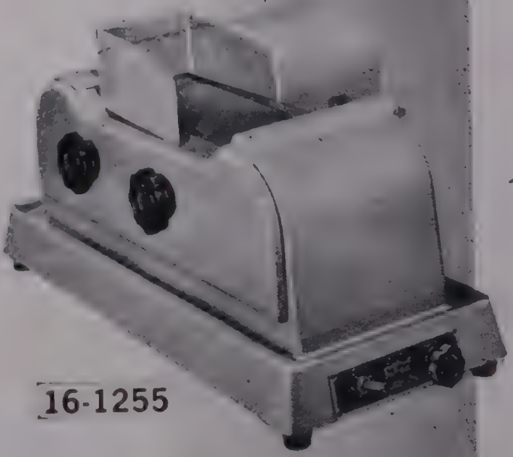

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AUGUST 1964

Micro-Metallurgy

THE discovery and subsequent development of numerous metals and alloys for diverse applications are the result of mankind's eternal quest for materials with improved performance. Increasing specialisation in this field of application of metals and emphasis on utilisation of indigenous resources call upon the metallurgical 'back room' boys to turn out new construction materials as expeditiously and economically as possible.

In this context considerable stress has been laid during recent years on micro-metallurgy which means the metallurgy of minute additions. During the past, many connected with the science and art of metallurgy have been fearful of the highly damaging effects of minor amounts of impurities, including gases, tramp elements and metalloids. The study of such damaging impurities has founded the basis of major programmes both on academic basis and on applied fields. In recent times, however, it has been realized that minute additions will confer extraordinary beneficial effects. In ferrous and non-ferrous metals and alloys, micro-additions of alloying elements have profoundly affected the resultant physical properties and metallurgical characteristics of the alloys. Some of the most striking cases are those of boron in acting on hardenability of steel when added to the extent of 10 to 30 parts in a million. Likewise, the highly beneficial effects of minute additions of aluminium introduced to the extent of 200 to 500 parts in a million are today well established. Cerium also greatly improves the oxidation characteristics of nickel-chromium alloys.

In India to day, the study of micro-metallurgy has special significance in academic fields as also in the background of limitations in reserves of some strategic raw materials. With a view to focus attention on multitudinous aspects of micro-metallurgy, a Symposium on 'Micro-Metallurgy' is being organised by the National Metallurgical Laboratory in February 1965 to discuss the role of minute additions to ferrous and non-ferrous metals and alloys, wherein the metallurgists, engineers, research workers, industrialists, consumers and planners can get together, exchange technical 'know-how', examine interrelated problems and discuss the various aspects of the subject matter.

Spectrochemical Determination of Antimony in Lead-Tin Solders

M. K. Ghose
P. C. Debnath
B. C. Kar

Spectrographic methods for accurate and rapid determination of both high and low antimony contents in solders have been discussed. Porous cup technique was adopted for estimation of high amount of antimony up to 10 per cent and oxide arc technique was adopted for antimony up to a lower limit of 0·001 per cent.

Analytical accuracy varied from 3 to 6 per cent of the amount present when the concentration of the element to be determined is low. At higher concentration, however, lower values were obtained for both precision and accuracy.

ESTIMATION of antimony in lead-tin solders by chemical methods is cumbersome, time-consuming and at times yields erratic results. Results obtained by spectrographic methods are more consistent and reliable. Applicability of the spectrographic method depends, however, upon the antimony content of the solder sample. There are generally two kinds of solders in common use, namely, antimonial solders and non-antimonial solders. Various techniques have been suggested by different workers for the determination of antimony in solder.

Jaycox[1,2] suggested two methods for estimation of low antimony, one in lead base alloys and the other in lead-tin solders by the dry powder D.C. arc technique using filters; he has also suggested a method of estimation of high antimony in tin base alloys by D.C. arc technique using filters[3]. Wiley, Cestaro and Dunn[4] have described a method for determining high antimony in antimonial lead alloy by the point-to-plane spark technique. Danko and Wiener[5] have described a method of spectrographic analysis of solders and babbits.

In the solid electrode method, samples and standards are generally used in the form of cast discs or any other flat surface suitable for sparking against a graphite electrode. To prepare the samples by casting so as to have the same structure as well as free from segregation is not an easy job.

In this paper, Porous Cup[6] technique of analysis for high antimony contents and oxide arc technique for low antimony content in solders have been described. For both the methods synthetic standards were used. In porous cup technique, both samples and standards were used in the form of solutions and in oxide arc technique, in the form of their oxides to get better homogeneity.

Experimental procedure

Estimation of high antimony in antimonial solders

The porous cup method provided for the determination of antimony from 1·0 to 10 per cent in tin-lead antimonial solder employing high voltage simple condensed spark excitation of the standard and samples in the form of solutions. The standards are prepared synthetically containing almost equivalent percentages of tin and lead, antimony varying from 1·0 to 10 per cent.

Spectra of the standards and the samples were recorded on a suitable photographic emulsion. Intensity ratios of a selected pair of analytical line of antimony and internal control lead line were determined photometrically. The concentration of antimony in the unknown samples was read from the analytical curve relating log intensity ratio to log concentration of antimony.

Standard samples

Standard solutions for tin and antimony were prepared separately by dissolving weighed quantities of spectroscopically pure materials in a mixture of (1 : 1) concentrated and extra pure hydrochloric and nitric acid in a low heat. Standard solution of lead was prepared by dissolving requisite amount of spectroscopically pure material in 1 : 1 (v/v) extra pure nitric acid. The solutions were then mixed in suitable proportions to make synthetic standards having percentages of antimony in different standards as indicated in Table I. Almost equivalent amounts of lead and tin are kept in each standard.

TABLE I. Antimony percentage in different standards

Standard Nos.	Antimony %
1	1·0
2	3·0
3	5·0
4	7·0
5	10·0

Test solutions

Filings of the test samples of lead-tin solders containing varying amounts of antimony were dissolved in a mixture of extra pure hydrochloric acid and nitric acid (1 : 1) at a low heat.

Electrodes

Porous cup was prepared by cutting a spectrographic graphite rod of 10 mm dia. into 3·8 cm pieces and drilling a 3 mm hole in them along the axis from one end to within 1·5 mm of the other end. With the help of a long nosed pipette, 1 to 2 ml of the solution to be analysed was inserted carefully into the cavity of the porous cup, which was used as an upper electrode with the

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Mr. M. K. Ghose, Senior Scientific Officer; Mr. P. C. Debnath, Junior Scientific Assistant; Dr. B. C. Kar, Assistant Director; National Metallurgical Laboratory, Jamshedpur.

open end up, so that no air bubbles remained inside the cup. During sparking, the solution diffused through the porous electrode slowly by wick action, constantly renewing the surface film of the solution. The lower electrode used was spectrographically pure carbon rod of 6 mm diameter tipped with an 80° cone.

Excitation

The samples were excited by a simple condensed spark, using a ¼ KVA transformer with a secondary tapping set to give 15 KV on open circuit. Capacitance 0·005 μF; added inductance 0·13 mH.

Apparatus and conditions of exposure

Hilger medium quartz spectrograph (E 498, flat field) was used. In order to obtain uniform intensity along the whole length of the spectrum line, the light from the source was focussed within the optical system of the spectrograph by means of a quartz spherical lens (Hilger F 1 026) placed at a distance of 2 cm away from the slit and 36 cm away from the source.

The following experimental conditions were also maintained :

Slit opening ...	0·02 mm	Slit length ...	2 mm
Spark gap ...	4 mm	Presparking	10 sec
Exposure ...	60 sec	Plate used ...	Kodak B10

Spectra of the standards and the unknown solutions were taken in the same plate. Care was taken to record the spectra of the unknowns and standards properly distributed on the plate keeping the conditions of exposure identical in all the cases.

Photographic processing

The plates were developed in 'Kodak—D 19 b' developer for 3 minutes keeping the temperature at 20°C (±1°) and fixed for 10 minutes. The temperature of the fixer was also maintained at 20°C (±1°). After careful and thorough washing, the plates were rinsed with distilled water and dried at room temperature.

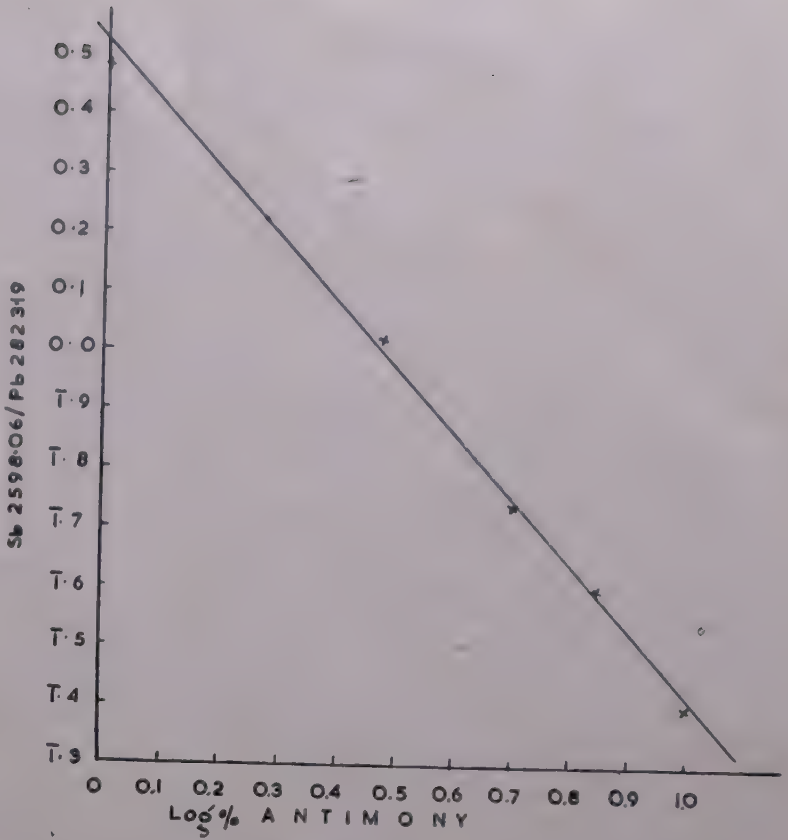
Density measurement

The density of the spectral lines was measured by Hilger non-recording microphotometer. The variable shunt of the galvanometer was adjusted to obtain a deflection of 500 mm for an unexposed portion of the plate (clear plate deflection). Working curve for antimony was drawn by plotting log microphotometer deflection of antimony line/log microphotometer deflection of lead line against log of known percentage of antimony. Table II shows the analytical line pairs used for preparing the working curve.

TABLE II Analytical line pairs

Analytical line, A	Internal standard line, A	Concentration range per cent
Sb 2 598·06	Pb 2 823·19	1·0–10·0

Figure 1 represents the working curve for antimony. From the working curve, concentration of antimony in the unknown solutions was determined by interpolation.



1 *Working curve for antimony [1·0–10·0%].*

Estimation of low amount of antimony

The oxide arc technique provided for the determination of antimony from 0·001 to 0·1 per cent in tin-lead non-antimonial solder. The dry oxide powder of samples and standards prepared synthetically were mixed with pure graphite powder and put into the crater of graphite cup electrode. The spectra of the standards and the samples were recorded on a suitable emulsion employing direct current arc as the excitation source. Intensity ratios of selected pairs of analytical line of antimony and internal standard lead line were determined photometrically. The concentration of antimony was read from an analytical curve relating log intensity ratio to log concentration.

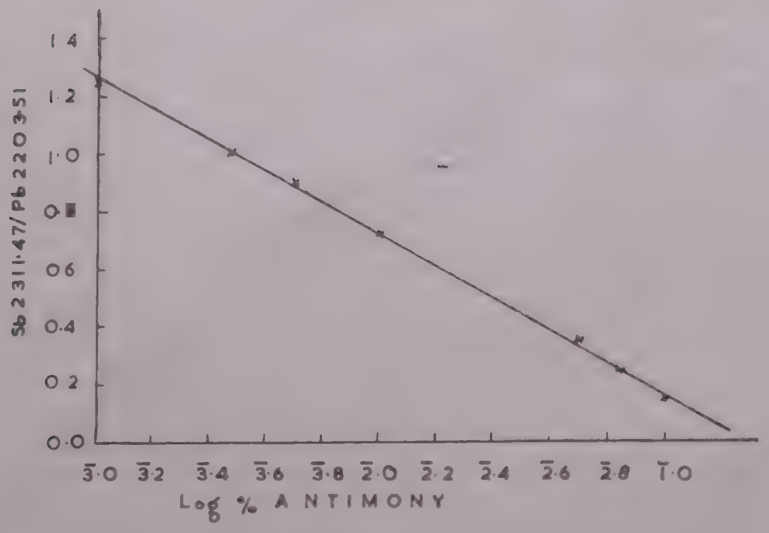
Standard samples

Table III shows the percentage of antimony present in the standards prepared synthetically. Lead and tin were kept almost equal in amount in all the standards.

TABLE III Antimony percentage in different standards

Standard Nos.	Sb%
1	0·001
2	0·003
3	0·005
4	0·01
5	0·05
6	0·07
7	0·10

For each standard, calculated amounts of spec. pure lead and tin to obtain one gram of material were placed in an evaporating dish. The mass was digested with a few ml of 1 : 1 (v/v) extra pure nitric acid on a hot plate. After digestion was complete, the required amounts of antimony solution were added by pipetting measured volume from the standardised antimony solution to ensure the concentration of antimony in different standards according to Table III. The standard antimony solution was prepared by dissolving spectroscopically pure antimony with extra pure concentrated sulphuric acid. A few ml of 1 : 1 (v/v) sulphuric acid were added to the whole mass to convert the salts to sulphates, which was evaporated to dryness; the evaporating dish



2 *Working curve for antimony [0·001–0.1%].*

was then placed in a muffle furnace and baked at 600°C for half an hour. The converted oxide was thoroughly ground in an agate mortar. This powdered oxide was subsequently mixed with equal parts of pure graphite powder. The standards were stored in air-tight bottles.

Preparation of unknown samples

2 gm of the representative sample was placed in an evaporating dish and digested with 1 : 1 (v/v) extra pure nitric acid. When digestion was complete, a few ml of sulphuric acid (1 : 1) were added. The mass was evaporated to dryness and baked in a muffle furnace at 600°C for half an hour. The converted oxide was thoroughly ground in an agate mortar and subsequently mixed with equal parts of pure graphite powder.

Electrodes

The lower electrode (anode) was a 10 mm dia. high purity graphite rod with a crater cut into the end to a depth of 2 mm. The upper electrode (cathode) was a 6 mm dia. high purity carbon rod with a flat end.

Apparatus and source of excitation

Hilger medium quartz spectrograph (E 498 flat field) was used. A spherical lens (Hilger F 1026) was placed at a distance of 2 cm away from the slit and 36 cm away from the source.

A d.c. arc with an open circuit potential of 220 volts was employed for excitation. The current was controlled by a series resistance.

The following experimental conditions were maintained :

Slit opening—0·01 mm ; slit length—2 mm ; arc gap—3 mm ; current—8 amps. ; arc preburn period—none ; exposure period—30 sec. ; plate used—Kodak B 10

Procedure

The crater of the lower electrode was filled up to the requisite level with the sample or the standard and the electrode system was aligned properly. The arc was struck by bringing into contact the upper carbon electrode which is the cathode with the lower electrode. The upper electrode was raised slowly upwards to a predetermined position to obtain an arc gap of 3 mm ; this gap was checked optically and maintained constant. The exposure was given for 30 seconds. Spectra of the standards and the unknowns were taken in the same plate. Care was taken to record these spectra properly distributed on the plate maintaining the conditions of exposure strictly identical in case of both standards and unknowns.

Photographic processing and density measurements are the same as described under the method of high antimony estimation. The analytical line Sb 2311.47 A and internal standard line Pb 2203.51 A were used for preparing the working curve. Figure 2 represents the working curve for antimony.

From this working curve, the concentration of antimony in the unknown is determined by interpolation.

Precision and accuracy

The precision of both the methods was determined by repeated tests on the same sample. The coefficient of variation was calculated from the relation,

$$\alpha = \frac{100}{C}\sqrt{\frac{\Sigma d^2}{n-1}},$$

where C=percentage of composition, d=difference of determination from the mean, n=number of determinations. The results of both the methods are given in Tables IV and V.

TABLE IV High antimony—Porous cup technique

Test samples	Actual content of Sb	Spectrographically estimated Sb %	Mean Sb %	Coeff. of variation
Synthetic No. 1	4·5	4·20 4·32 4·28 4·38	4·35	±3·57
Synthetic No. 2	7·8	7·60 7·94 8·10 8·10	7·93	±3·02
Synthetic No. 3	9·5	9·20 9·55 9·33 9·40	9·37	±1·53
Soft solder 'A'	2·8	2·62 2·70 2·55 2·90	2·69	±3·11

TABLE V Low antimony—Oxide arc technique

Test samples	Actual content of Sb	Spectrographically estimated Sb %	Mean Sb %	Coeff. of variation
Synthetic No. 4	0·008	0·0076 0·0072 0·0079 0·0083	0·0077	± 5·76
Synthetic No. 5	0·03	0·026 0·029 0·026 0·033	0·028	±10·96

Discussion

In this work, oxide arc technique has been adopted for determination of antimony from 0·001 to 0·1 per cent and porous cup technique for antimony from 1·0 to 10·0 per cent. For the determination of antimony from 0·1 to 1·0 per cent, porous cup technique also can, however, be adopted with 2 minutes' exposure and maintaining all the other conditions identical as described before.

If iron is present in the solder, Sb 2598·06 A may not be well resolved with Fe 2598·36 A when medium quartz instrument is used. In such a case, large quartz spectrograph having a greater resolving power may be used.

Acknowledgement

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Chromate Passivation of Zinc

S. Rao Addanki
A. K. Lahiri

The paper describes the results obtained on chromate films formed on zinc, zinc plated steel and galvanised steel, by dipping in acidified sodium dichromate solutions. The work covers the effect of solution composition and time of immersion, etc. on the weight of the film formed and metal attacked and also on the characteristics of the film formed. The protective property of the film has been determined by salt spray test and humidity test.

The results indicate that the acid content of the solution primarily affects the properties af the film formed in solution containing 200 gm/l of sodium dichromate. Acid content above 12·5 c.c./l was found to give loose film which had lower protective property. Of the three types of zinc, zinc plated steel possessed maximum resistance and galvanised steel the least.

PROTECTION of metal against deterioration due to corrosion is carried out to a great extent by application of organic or inorganic coating. In addition to these methods, protection by chemical conversion coatings generally consists in modifying the metal surface such that the coating becomes an integral part of the metal, making the bond between them very strong. This type of coating generally acts as a barrier between the metal and the environment. In addition these coatings also lend themselves to easy impregnation with oils, grease, paints, lacquers, etc.

In the outdoor atmosphere zinc corrodes slowly and uniformly at a rate largely controlled by the corrosive conditions. The thin grey film of corrosion product formed on the surface plays no real part in controlling corrosion. However under humid conditions and with a stagnant film of water with limited access of oxygen, (e.g. under indoor conditions), a non-uniform type of corrosion develops resulting in the formation of bulky film of white corrosion product. Zinc, exposed to such corrosive conditions, can be given improved corrosion resistance by chromate passivation, whereby a thin coloured film is produced. The coating can be given either by simply dipping or by electrolytic treatment by making the sample an anode. The film formed according to Anderson[1] is $Cr_2O_3 . CrO_3 xH_2O$ or $Cr(OH)_3\ Cr(OH)\ CrO_4$.

It is generally presumed that the protective value of the film is due to the release of hexavalent chromium to water which comes in contact with it though according to Clarke and Andrew[2] the value of the film as an inert protective layer plays also an important role.

Of the various processes, the dip process is of considerable importance and the important industrial patented processes of this type are known as Cornak, Rushtol, etc. The dip solutions in general contain soluble chromates or dichromates and acids, namely, sulphuric, hydrochloric or nitric acid. However, the salt and acid most commonly used are sodium dichromate and sulphuric acid respectively.

The formation of films and their protective value have been shown by previous workers to be largely influenced by the amount of acid, time of treatment and temperature of treatment. Clarke and Andrew[2] have carried out detailed investigation on the effect of various variables on the chromate passivation of pure zinc sheet and zinc plated steel in different solutions. They have shown that dichromate content can be varied between 50 and 200 gm/l without appreciable effect. However they have found a marked effect of sulphuric acid in the range of 1·2–24 ml/litre on the formation of chromate film.

No such detailed studies have however been carried out with galvanised steel. The present investigation was, therefore, taken up to study the effect of various variables on chromate film formed on galvanised steel and their corrosion resistance properties. In addition to galvanised steel, zinc and zinc plated steel were also used for collecting data which can be compared with those obtained with galvanised steel.

Materials for testing

The following materials were used for conducting the tests.

Rolled zinc: The tests were carried on 2″×2″ pieces of rolled zinc sheet of composition Pb—0·886%, Cd—0·066% and Zn rest. The samples were polished to a finish by 'O' emery paper and degreased, using MgO paste.

Zinc plated steel: Bright polished 1½″×4″ mild steel sheets were electro-plated with an ordinary smooth, nonlustrous coating of zinc from cyanide bath, and then rinsed in water. The samples were degreased with MgO paste prior to treatment. The zinc plating was carried out under the conditions given in Table I.

TABLE I Bath composition for zinc plated steel

Zinc cyanide	59 gm
Sodium cyanide	53 gm
Caustic soda	44 gm
Sodium carbonate	9·5 gm
Aluminium sulphate	4·7 gm
Water	One litre
Temperature	Room temperature
Time	20 min
Current density	2·15 amp./sq dm

Galvanised steel: The 2″×2″ samples of galvanised steel were cut from hot dipped galvanised sheets having a coating weight of 1·507/sq ft. The 'as received' samples were in good condition and were degreased with MgO paste prior to testing.

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Experimental procedure

Solution: The chromate solution was prepared by dissolving 200 gm of sodium dichromate per litre of water. To this solution concentrated sulphuric acid (Sp. gr. 1·86) was added in ranges, varying from 5 c.c. to 40 c.c./litre.

Change in weight

The studies were carried out to determine effect the of different variables on attack on zinc and weight of film formed. The samples were weighed before and after treatment. The film formed was then removed by dissolving the same in 20% pure chromic acid at 90°C by one minute immersion, as recommended by Clarke and Andrew.[2] According to them, this treatment has only a minute attack on the zinc base and so the error introduced thereby can be neglected. The loss in weight of the treated specimen after dissolving the film gave the weight of the film. Further, the difference between weight of the specimen before chromate treatment and after stripping the film, gave the extent of attack on zinc

Description of the chromate process

All the samples, after degreasing, were weighed and then given a pre-chromating treatment by treating them in a boiling solution containing 6 oz of trisodium phosphate per gallon. Treatment for three minutes in the above solution was found to be sufficient for the purpose. Treatment of longer duration however gave a black film on the surface. This treatment has been recommended as a pretreatment and does not involve any phosphating of zinc. The pretreated samples after drying were weighed and then dipped in chromating solution for a specified time, removed and rinsed thoroughly in running water. The samples were dried by blowing cold air. The samples after treatment were weighed and then treated to strip off the film whenever necessary. All the tests were carried out at room temperature which was 25±3°C.

Results

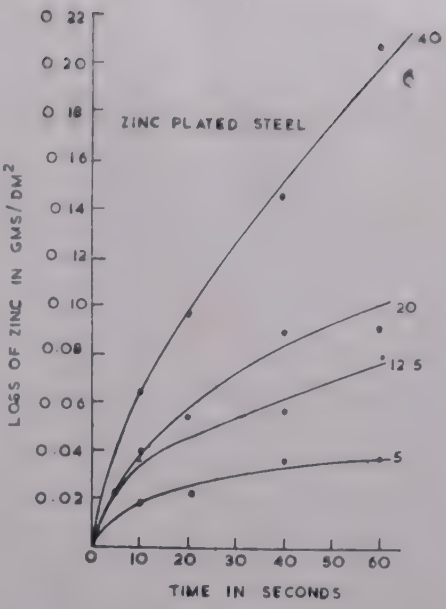
Effect of sulphuric acid content

The effect of variation of sulphuric acid content, in steps from 5–40 c.c./litre and keeping sodium dichromate content at 200 gm/litre, on the weight of zinc attacked and weight of film formed have been plotted for different periods of immersion in Figs. 1 to 6.

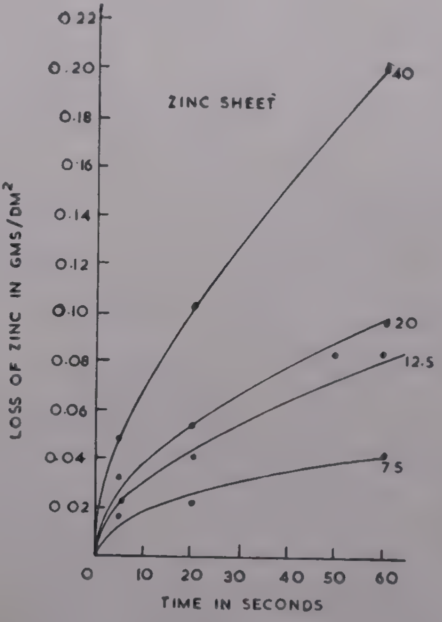
The acid content of the solution was found to have considerable influence on the weight of coating. While the attack on basis zinc went on increasing with acid content, the weight of the film produced passed through a maximum. This is in agreement with the observation of Clarke and Andrew[2] who showed a slight decrease in weight of the film formed on increasing acid concentration from 12·5 c.c./l to 20 c.c./l. In the present studies use of still higher acid concentrations up to 40 c.c./l showed further decrease in weight of the film formed. The acid concentration, where the film weight reached a maximum, varied with the type of materials used. Use of higher acid concentration decreased the weight of the film formed and caused vigorous evolution of hydrogen. The solution also turned dark red indicating the accumulation of trivalent chromium in the solution.

Effect of time of treatment

The weight of the zinc attacked and the weight of the film formed were found to increase rapidly for the first few seconds. With further increase in time of immersion the weight of the zinc attacked went on increasing but with a reduced rate. Up to immersion period of sixty seconds as done in this investigation, the rate of increase in weight of the film formed was however found to decrease considerably with increase in period of immersion, so much so that at higher acid concentrations the weight of the coating remained constant after the initial increase.



1 *Weight of zinc attacked in solutions of different acid concentration.*



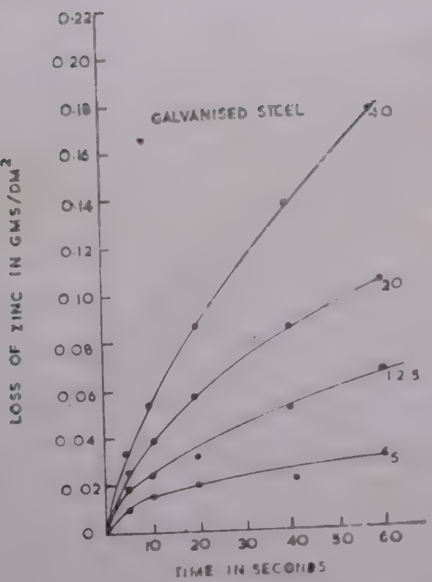
2 *Weight of zinc attacked in solutions of different acid concentration.*

Effect of type of coating

The overall change in weight, as a result of chromate treatment, was found to be very small for rolled zinc, zinc plated steel and galvanised steel treated in solutions containing lower concentration of acid indicating that the weight of the film formed is nearly equal to the amount of zinc attacked. With higher acid concentrations the amount of film so formed was found to be disproportionate to the attack on zinc resulting in overall decrease in weight. This indicated that with increase in acid concentration the attack on zinc is more than the weight of the film formed.

The weight of the film formed was found to be maximum for zinc plated steel while not much difference was observed between rolled zinc and galvanised steel.

The concentration of acid at which the film weight reached a maximum varied with type of zinc tested. The



3 *Weight of zinc attacked in solutions of different acid concentration.*

concentrations observed for various types of material tested are given below :

(*a*) Rolled zinc	12·5–20 c.c. of H_2SO_4/l
(*b*) Zinc plated steel	12·5–20 ,, ,,
(*c*) Galvanised steel	20–40 ,, ,,

Nature of film formed

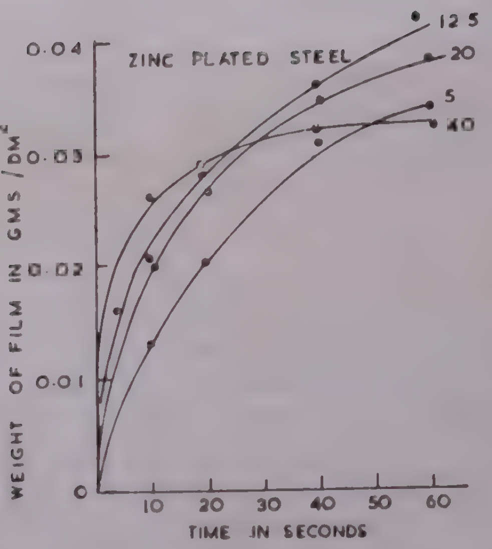
The appearance of the chromate film formed varied with the time of treatment, acid concentration and type of material. Acid concentrations up to 12·5 gm/l and treatment time up to 10 sec gave an iridescent film showing hues of greenish, yellow or reddish colour for both zinc plated steel and rolled zinc. These colour effects would appear to be mainly due to the interference of colours of very thin transparent film. The colour on rolled zinc was however duller in nature. With increase in time of immersion and acid concentration, the film appearance passed through a yellow brassy stage ultimately becoming brown powdery. The galvanised steel did not show any iridescent film except for treatment up to 5 sec in solution containing up to 7·5 c.c./l of H_2SO_4. The colour on these was yellow and passed ultimately to brown depending on the concentration of acid and the time of immersion.

The adhesion of the film was tested by giving the surface a single rubbing with a fragment of smooth white writing paper with the tip of the finger. The iridescent films were found to be less adherent while the brown films were poorly adherent. Brassy films on galvanised steel were found to be less adherent than those on rolled zinc or zinc plated steel.

Salt spray test

Salt spray tests were carried out on samples suspended in salt spray chamber at room temperature, which varied between 28±3°C during the test period. The tests were carried out under intermittent conditions with daily spraying time of 7 hours. For the remaining period of 17 hours the specimens were allowed to remain inside the chamber.

The conditions of the specimens were examined periodically during salt spray test. With time, the yellow colour of the film was found to disappear. This disappearance of the yellow colour was rapid with samples treated for periods of shorter duration. However the disappearance of the colour of the film was not found to impair the protective value of the film immediately as even after the entire colour had been leached out, the protection of zinc from corrosion was found to persist. Samples treated for 20 sec showed better resistance to corrosion than those treated for 5 or 60 sec. This was specially more marked in case of galvanised steel than zinc as will be evident from Table II. From the salt spray studies it will be clear that in addition to weight of coating, nature of film is also important. Samples having the same film weight but different in nature of film showed different protective properties. Thus samples treated for 20 sec in solution containing 7·5 c.c./l of sulphuric acid showed better protective property than the same treated in 40 c.c./l of sulphuric acid, in spite of their film weight being the same.



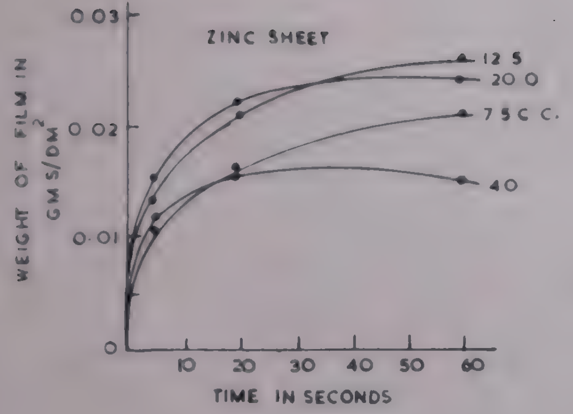
4 *Weight of chromate film formed in solutions of different acid concentration.*

Effect of heating the specimens

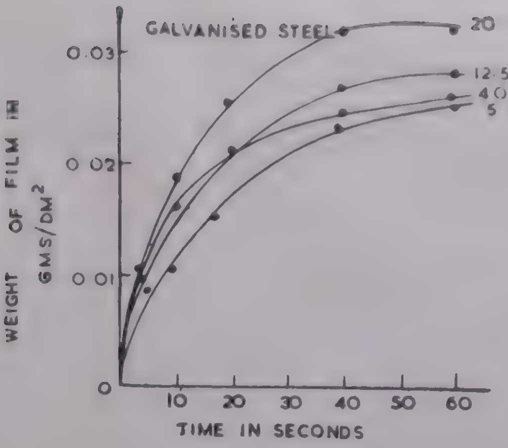
Anderson[1] and Clarke and Andrew[2] have pointed out that the film should not be heated to avoid deterioration of its protective properties. To illustrate the ill effect of heating, salt spray test was carried out on galvanised steel

TABLE II **Typical salt spray test data on chromate treated zinc and galvanised steel**

Sl. No.	Material	Tretment Solution	Time in sec	Time for appearance of first white corrosion product in days
1.	Zinc	$Na_2Cr_2O_7$–200 gm/l H_2SO_4–7·5 c.c./l	5	6–7
2.	,,	,,	20	10–11
3.	,,	,,	60	7–8
4.	,,	$Na_2Cr_2O_7$–200 gm/l H_2SO_4–40 c.c./l	5	6–7
5.	,,	,,	20	5–6
6.	,,	,,	60	5–6
7.	,,	(without treatment)		6–7 hr
8.	Galvanised steel	$Na_2Cr_2O_7$–200 gm/l H_2SO_4–7·5 c.c./l	5	7–8
9.	,,	,,	20	9–10
10.	,,	,,	60	6–7
11.	,,	$Na_2Cr_2O_7$–200 gm/l H_2SO_5–40 c.c./l	5	6–7
12.	,,	,,	20	6–7
13.	,,	,,	60	4–5
14.	,,	(without treatment)		6–7 hr
15.	Zinc plated steel	$Na_2Cr_2O_7$–200 gm/l H_2SO_4–7·5 c.c./l	5	9–10
16.	,,	,,	20	16–18
17.	,,	,,	60	16–18
18.	,,	$Na_2Cr_2O_7$–200 gm/l H_2SO_4–40 c.c./l	5	16–18
19.	,,	,,	20	12–14
20.	,,	,,	60	12–14



5 *Weight of chromate film formed in solutions of different acid concentration.*



6 *Weight of chromate film formed in solutions of different acid concentration.*

and rolled zinc. The treated specimens were heated for one hour at 60°C, 100°C and 200°C. The effect of heating was found to be quite pronounced on the appearance of film. Heating at 60°C had no effect on colour of the film. Samples heated at 100°C and 200°C however darkened and acquired a dark grey colour. The film which was adherent, became loose on heating. The heated samples were tested in salt spray chamber with intermittent spraying as described previously. The result of the tests is given in Table III for zinc and galvanised steel. Results indicate that by heating, the protective value of the film is deterioated considerably.

Of the galvanised steel and zinc samples, the latter showed better corrosion resistane than the former. However for both the materials the white spots indicated corrosion which developed within 24 hours for samples heated at 100°C and 200°C.

Humid atmosphere test

The humidity test was carried out in 'Gallenkamp' humidity oven. The condition involved condensation of fine water droplets on the surface of the specimen. The specimens were daily exposed to 98·5% humidity at 48°C for 7 hours. The condensation of the water droplet was accomplished by bringing down the temperature in the cooling cycle. The two cycles thus consisted of 7 and 17 hours respectively each day. The cyclic test was continued for 30 days. The result showed that untreated zinc develops white rust within 48 hours. The treated samples, on the other hand, were found to be free from corrosion even after 30 days. In humidity test, no difference in behaviour between zinc plated steel and galvanised steel was observed.

TABLE III Salt spray test data on chromate treated samples heated at different temperatures

Solution: $Na_2Cr_2O_7$—200 gm./l H_2SO_4—7·5 c.c./l

Material	Time of treatment in sec	Temp. of heating in °C	Time of heating in min	Time for appearance of first white corrosion product in days
Zinc	10	R.T.	—	10–11
	60	R.T.	—	8–9
	10	60	60	10–11
	60	60	60	11–12
	10	100	60	1–2
	60	100	60	1
Galvanised steel	10	R.T.	—	8–9
	60	R.T.	—	6–7
	10	60	60	8–9
	60	60	60	7–8
	10	100	60	1
	60	100	60	1
	10	200	60	1
	60	200	60	1

Discussion

The mechanism of chromate film is based on the formation of insoluble chromium salts at the metal surface. The acidic solution used for the purpose attacks the base metal which results in the pH of the solution at the metal/solution interface to increase. This causes the reduction of hexavalent chromium to trivalent state. At a critical pH the trivalent chromium and some hexavalent chromium are co-precipitated on the metal surface.

It is therefore quite natural that for a good treatment bath, the solution composition is important. If the pH of the solution at the interface does not increase considerably, the film formation will be hampered. Moreover the film formed may be redissolved if the acid concentration at the interface increases. Both these will reduce the amount of trivalent chromium entering the film and will cause a build-up of trivalent chromium in the solution.[4]

The results obtained in the present investigation clearly indicate the profound influence of the acid concentration in controlling the film formation. At acid concentrations between 5–10 c.c./l, the amount of film formed was found to be nearly similar to the amount of zinc attacked indicating that at these concentrations the pH at the metal/solution interface is optimum for formation of a good film. An increase in acid concentration resulted in the pH at the interface to increase and so resulted in the amount of zinc attacked to be much more when compared to the amount of film formed. The decrease in the weight of the film formed with longer immersion periods, for higher acid concentration, is on the other hand due to the dissolution of the film formed.

The protective property of the film was found to be dependent on the treatment. A thin iridescent or yellow film gave better protection than loose non-adherent ones. This will be further evident from the fact that films on zinc plated steel and rolled zinc showed an overall higher resistance to corrosion than that on galvanised steel. The effect of heating was found to destroy the protective properties of the film considerably. However even after heating to 200°C, the treated samples were found to have higher resistance to corrosion than untreated ones. This is probably due to the fact that, though during heating the film loses moisture and the soluble chromium becomes insoluble[3,5], the value of the film as an inert protective layer is retained to some extent.

Conclusions

On the basis of different tests carried out it may be concluded that:

(i) Chromate passivation greatly increases the resistance to corrosion of zinc.

(ii) The properties of the film formed is dependent mainly on acid concentration. Acid content above 12·5 c.c./l reduces the amount of the film formed and also deteriorates its protective properties.

(iii) The film formed on galvanised steel is in general less adherent than that on zinc and zinc plated steel.

(iv) Heating reduces the protective property of the film probably due to its dehydration and loss of soluble chromate.

(v) Of the type of zinc and zinc coatings studied, corrosion resistance effect of chromate treatment was found to be most prominent for rolled zinc and least for galvanised steel.

Recommended procedure

On the basis of these studies the following procedure can be recommended for chromate passivation of zinc:

(i) The parts to be treated should be thoroughly degreased and should then be given a pretreatment in a boiling solution containing 40 gm of trisodium phosphate per litre

(ii) The composition of the solution for good treatment is as follows:
Sodium dichromate—150–200 gm/l; H_2SO_4 (sp. gr. 1.84) 5–10 c.c./l. Time of treatment 10–20 sec.

(iii) Heating of the film or treating with hot water should be avoided as they reduce protective value.

Acknowledgement

The authors' thanks are due to Dr T. Banerjee, Deputy Director, National Metallurgical Laboratory for his helpful suggestions during this investigation. Thanks are also due to Dr B. R. Nijhawan, Director, National Metallurgical Laboratory for his keen interest and valuable comments.

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Rapid method for the determination of manganese in the manganese-bearing stainless steel

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H. P. Bhattacharya

A rapid routine method for the determination of manganese in presence of high chromium had been developed which did not require the prior separation of manganese from chromium. This was possible by oxidizing both chromium and manganese by amonium persulphate in presence of 3–4% (V/V) H_2SO_4 and 4% (V/V) phosphoric acid and silver nitrate as catalyst and determining both the total permanganate equivalent for chromium and manganese and that for chromium alone. The amount of manganese present was then calculated from the difference between the two titres. The method has been successfully applied in the analysis of manganese-bearing stainless steel and is equally applicable to other alloy steels containing appreciable amounts of both chromium and manganese.

NICKEL free stainless steel developed in the National Metallurgical Laboratory contains high percentages of both chromium and manganese. The determination of manganese in the presence of small amounts of chromium (about 3%) does not present any serious difficulty and standard methods exist for the purpose. But when the steel sample contains a high percentage of chromium it is necessary to separate chromium first for the determination of manganese by standard bismuthate[1] or persulphate[2] method. The separation of manganese from chromium is effected generally by bicarbonate or by zinc oxide emulsion. This procedure requires considerable time for manganese determination as the chromium is first to be percipitated, made up to volume, settled and filtered. To avoid this time lag, a rapid routine method for the determination of manganese in the high manganese stainless steels was developed. Experiments were carried out to find out the optimum concentration of sulphuric acid for complete oxidation of both chromium and manganese in the presence of 4% (V/V) phosphoric acid. It was found that 3–4% (V/V) H_2SO_4 (conc.) was necessary for the complete oxidation of both chromium and manganese in presence of 4% (V/V) phosphoric acid. Estimation of chromium and manganese with optimum acid concentration was done by varying the ratio of manganese to chromium from 10 : 1 to 1 : 25 and satisfactory results were obtained. The values of chromium and manganese obtained compared favourably with those obtained by other standard methods. In this procedure the manganese was determined by deducting the permanganate equivalent of chromium from the total permanganate required for chromium and manganese and the time required for the determination of manganese was much less than that required by other methods. Both chromium and manganese could be determined in about 45 minutes.

Experimental procedure

Preparation of solution

(i) Standard chromium solution : One gram of pure chromium metal was dissolved in dil. H_2SO_4 and made up to one litre with water. From analysis it was found that 25 ml of this solution contained 0·0248 g. of Cr.

(ii) Standard manganese solution : One gram of pure manganese metal was dissolved in dil. H_2SO_4 and made up to one litre with water. From analysis it was found that 25 ml of this solution contained 0·0247 g of Mn.

(iii) Ferrous ammonium sulphate solution N/10 approx.

(iv) Standard $KMnO_4$ solution (N/10) : Standardised against standard sodium oxalate solution (N/10).

(v) Silver nitrate solution : 1% (W/V).

(vi) Ammonium persulphate solution : 25% (W/V) freshly prepared.

(vii) Phosphoric acid : Sp. gr. 1.70.

(viii) Sulphuric acid : Sp. gr. 1.84.

(ix) Hydrochloric acid : 1 : 3.

Determination of optimum sulphuric acid concentration necessary for oxidation

To find the optimum sulphuric acid concentration necessary for the complete oxidation of chromium and manganese the following experiments were carried out :

25 ml of either chromium or manganese solution was taken in an Erlenmeyer flask, 10 ml of phosphoric acid, 10 ml of silver nitrate solution (1%) and 7·5 ml to 25 ml of concentrated sulphuric acid were added and the volume was made up to about 235 ml with hot water. 15 ml of ammonium persulphate solution (25%) was added and the solution was boiled for 12 to 15 minutes. The flask was cooled in ice, excess ferrous ammonium sulphate solution (N/10) was added and the excess was back titrated with (N/10) permanganate solution. The amount of chromium or manganese was calculated from the permanganate equivalent of ferrous ammonium sulphate consumed. The results obtained are given in Table I.

It could be seen from the table that while the oxidation of chromium was complete in presence of 7·5 ml to 18

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TABLE I Effect of sulphuric acid concentration on the oxidation of chromium and manganese by ammonium persulphate method

Phosphoric acid	10·0 ml
Silver nitrate	10·0 ml
Ammonium persulphate	15 ml (25%)
Final volume	250 ml
Period of boiling	12–15 minutes

No. of expt.	Sulphuric acid added	Cr (gm) Taken	Found	Error (gm)	No. of expt.	Mn (gm) Taken	Found	Error (gm)
1.	7·5 ml	0·0248	0·0249	+0·0001	6.	0·0247	0·0248	+0·0001
2.	10·0 ml	0·0248	0·0249	+0·0001	7.	0·0247	0·0245	—0·0002
3.	12·5 ml	0·0248	0·0248	0·0000	8.	0·0247	0·0238	—0·0009
4.	18·0 ml	0·0248	0·0247	—0·0001	9.	0·0247	0·0160	—0·0087
5.	25·0 ml	0·0248	0·0240	—0·0008	10·	0·0247	0·0120	—0·0127

TABLE II Determination of manganese in presence of varying amounts of chromium

No. of expt.	Cr (gm) Added	Found	Error (gm)	Ratio Cr/Mn	Mn (gm) Added	Found	Error (gm)
1.	0·0248	0·0247	—0·0001	1 : 1	0·0247	0·0249	+0·0002
2.	0·0124	0·0125	+0·0001	1 : 2	0·0247	0·0249	+0·0002
3.	0·0050	0·0049	—0·0001	1 : 5	0·0247	0·0243	—0·0004
4.	0·0025	0·0025	+0·0000	1 : 10	0·0247	0·0244	—0·0003
5.	0·0248	0·0247	—0·0001	2 : 1	0·0124	0·0125	+0·0001
6.	0·0248	0·0248	0·0000	5 : 1	0·0049	0·0050	+0·0001
7.	0·0248	0·0247	—0·0001	10 : 1	0·0025	0·0025	0·0000
8.	0·0248	0·0246	—0·0002	25 : 1	0·00098	0·0010	+0·00002

ml H_2SO_4 per 250 ml solution, complete oxidation of manganese took place up to 10 ml of H_2SO_4 per 250 ml solution only. With excess of acid, oxidation of bivalent manganese to heptavalent manganese did not proceed to completion.

Determination of manganese in presence of chromium

Experiments were then carried out to find if manganese could be determined in presence of chromium by varying the ratio of manganese to chromium from 10 : 1 to 1 : 25. The procedure outlined before was followed keeping the concentration of H_2SO_4 3–4% (V/V). Permanganate equivalents of both the total manganese and chromium and that of chromium alone were determined and the amount of manganese present was calculated from the difference of the two titres. The results are given in Table II.

It will be found from the above table that manganese can be satisfactorily determined even in presence of twenty-five times its weight of chromium.

Determination of manganese in manganese-bearing stainless steels

Each of 0·1 g. of the stainless steel sample was weighed and transferred to 500 ml Erlenmeyer flasks and dissolved in 25 ml (1 : 2) sulphuric acid. The carbides were decomposed by dropwise addition of nitric acid and the nitrous fumes were driven off by boiling. 10 ml of phosphoric acid was then added to the flasks, the solutions were diluted to about 225 ml with hot water and 10 ml of silver nitrate (1%) solution was added in both the flasks. To each of the warm solutions 15 ml of ammonium persulphate solution (25%) was added, the contents were raised to boiling and boiled vigorously for 12 to 15 minutes. One of the flasks was removed from the source of the heat and cooled rapidly in ice. To the other flask, 5 ml of dil. HCl (1 : 3) was added and boiled till the permanganate colour was destroyed. It was then cooled rapidly in ice.

To each of the two flasks measured quantity of ferrous ammonium sulphate solution was added till there was an excess of at least 5 ml of ferrous ammonium sulphate solution. The excess ferrous ammonium sulphate present in both the solutions was titrated back with the standard permanganate solution (N/10). A blank for the amount of the ferrous ammonium sulphate solution used was found out. From the permanganate equivalent of the solutions, the percentages of chromium and manganese were calculated. The time required for the determination of both chromium and manganese was between 40–45 minutes. The results obtained are given in Table III.

TABLE III Determination of chromium and manganese in manganese-bearing stainless steel

No. of Expts	Cr% by persulphate method	Mn% by bismuthate method	Cr% by the investigated method	Mn% by the investigated method
1.	21·04	13·40	20·90	13·30
2.	21·10	13·60	20·97	13·45
3.	21·10	13·80	20·90	13·79
4.	23·28	14·20	23·23	14·01
5.	21·10	14·00	20·98	13·80
6.	22·07	16·70	21·97	16·90
7·	17·91	16·93	17·80	16·83
8.	17·50	12·72	17·40	12·81
9.	17·20	11·81	17·30	11·90
10.	20·90	13·01	20·81	12·91

It will be seen from the above results that the chromium and manganese contents of manganese-bearing stainless steels obtained according to this precedure compared favourably with those obtained by other standard methods.

Conclusion

From the experimental observation it was found that manganese could be determined rapidly in manganese-bearing stainless steels without separation of chromium by the procedure recommended here. It can be equally applied to other ferrous alloys containing high percentages of both chromium and manganese. The time required for the determination of both the constituents is about 45 minutes.

Acknowledgement

The authors wish to thank Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, for his interest and Dr T. Banerjee, Deputy Director, National Metallurgical Laboratory for his valuable comments and suggestions.

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A prototype vertical kiln for continuous thermal beneficiation

M. J. Shahani

A novel vertical column kiln has been designed for continuous processing of two-phase solids-gas systems. This column has a rated capacity of one tonne per hour and is particularly suited to the continuous thermal beneficiation of low grade ores in the field of mineral dressing.

IN the field of mineral dressing, thermal beneficiation of low grade ores is fequently necessary, prior to further dressing, to obtain desired concentrates. This normally involves two-phase solid-gas processing. Several processes such as fluidized bed, counter-current systems, co-current systems, and pulse columns have been developed and utilized to advantage. Some of these may be carried out either vertically or horizontally. The engineering of these systems encounters several serious problems such as chanelling of the gases through the bed of solids, bed hanging, etc. which lead to low overall process efficiencies. These drawbacks need to be minimized by appropriate engineering and design.

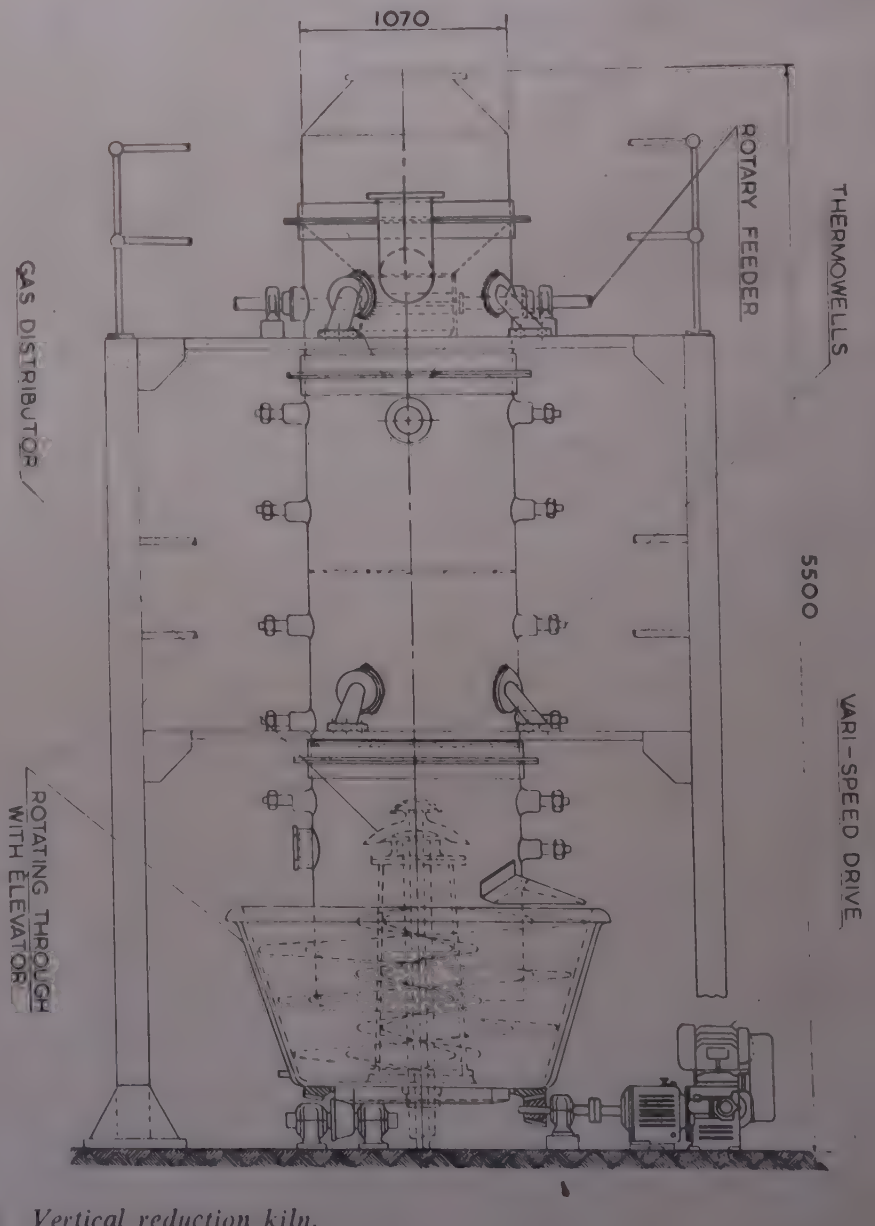
For the processing of lumpy ores such as low grade ferruginous manganese ores with reducing gases (magnetic reduction roast)[3] at temperatures of 500°C to 600°C, a novel type of vertical kiln has been developed. A counter-current plug flow system has been adopted as the basic process and various features (patented)[1, 2] have been incorporated to achieve conditions approaching plug flow and to minimize bed hanging and chanelling in order to ensure uninterrupted operation.

The process

Raw material, suitably sized to suit process conditions, is fed into the six metres high vertical column via a vari-speed roll feeder and is permitted to descend by gravity to fill the column and form a packed bed of porosity which is a direct function of particle size and shape in the main, with density and bed height as other contributory factors.

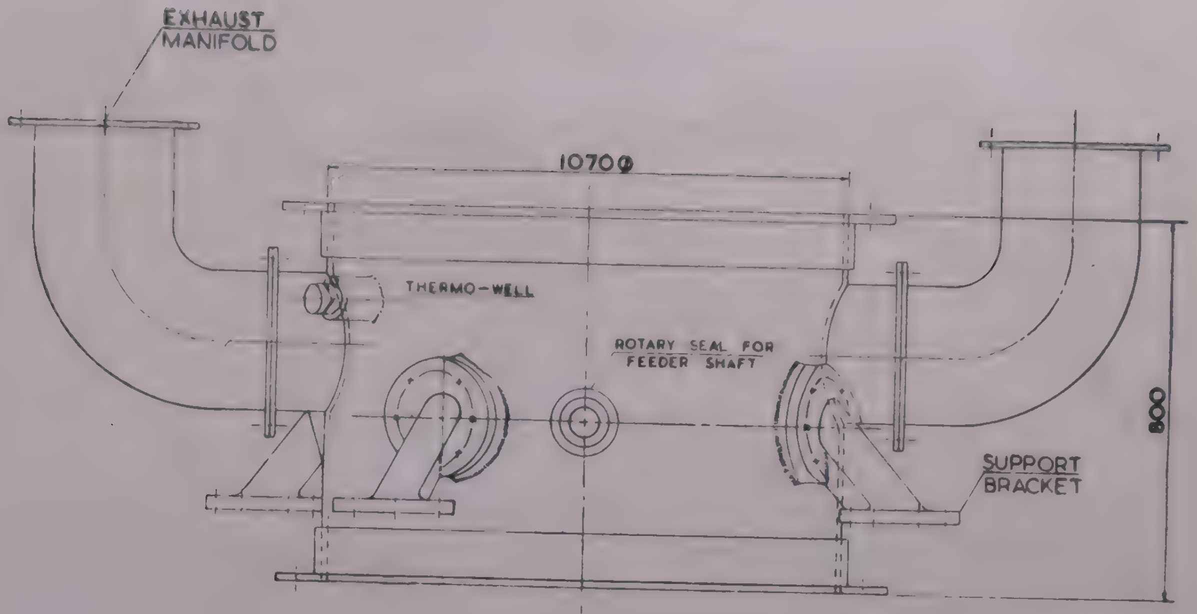
The processing gas, such as producer gas or coke oven gas, is introduced at the base of the kiln via a rotating distributor head. It ascends through the bed to process the packed solid particles and on to the exhaust manifold en route to the exhaust stack or dust collector/scrubber unit for recirculation by dilution of the main gas feed. The bed of solids, while being replenished by the feeder at pre-set desired rates, moves downwards continuously in plug flow fashion counter-current to the ascending gases till it enters the rotating water seal trough into which the lower end of the stationary vertical column dips. The rotating trough has been equipped with a screw spiral which elevates the processed solids to the top of the trough for onward conveying to the next process such as drying, etc. The water seal is continuously replenished by a water spray manifold located above the rotating trough lip. The spray nozzles are directed towards the stationary shell which is thereby cooled by the water running down its sides into the trough.

To start the reaction, the gases are ignited either by remote control or through ignitor ports located at the level of the gas distributor head. The exothermic reaction is regulated to temperatures around 600°C. Thermowells are located at frequent intervals along the entire height of the column to yield data on the temperature gradients within the column as also to locate and control the reaction zone. Pressure gauges and suitable

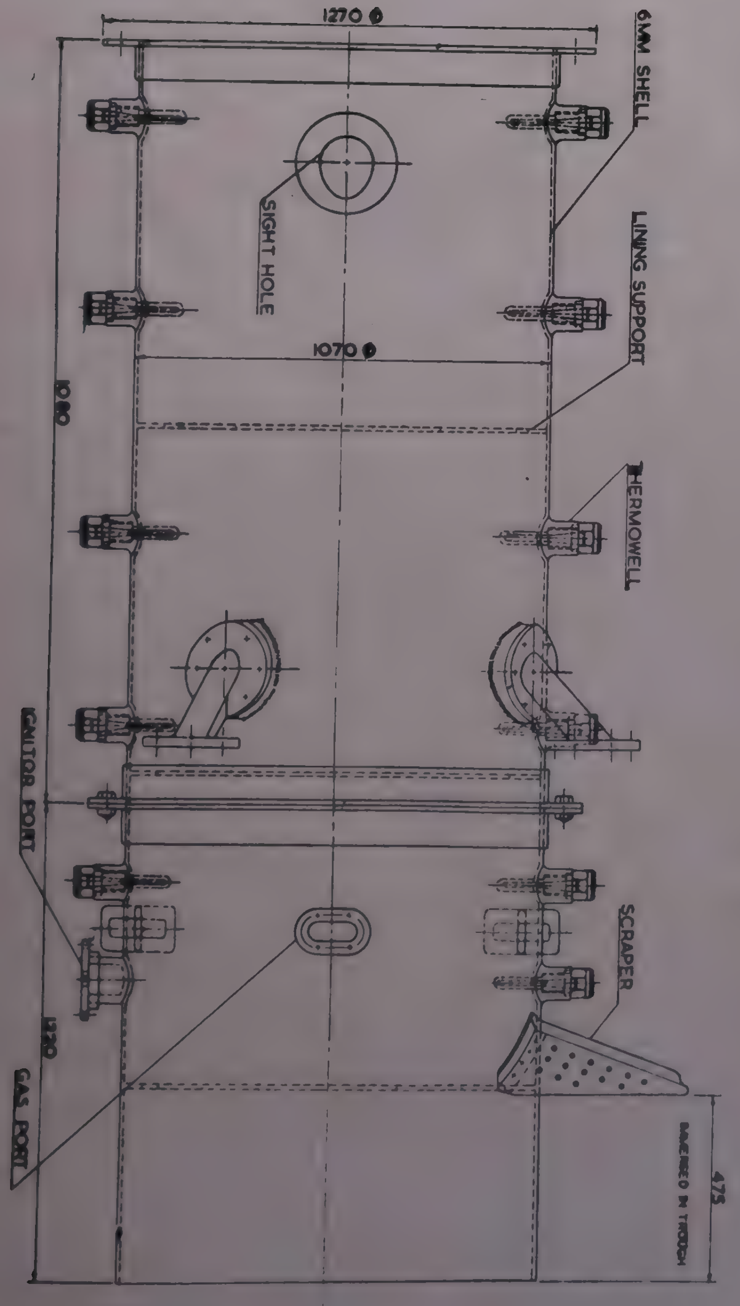


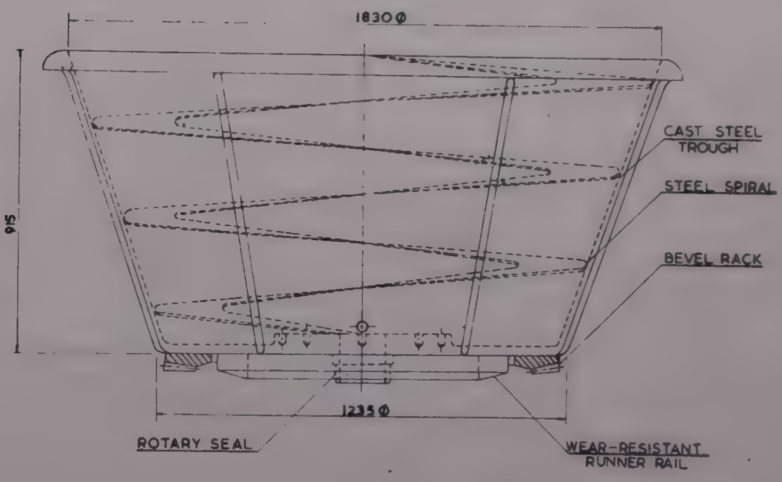
1 *Vertical reduction kiln.*

Mr M. J. Shahani, Assistant Director, National Metallurgical Laboratory, Jamshedpur.

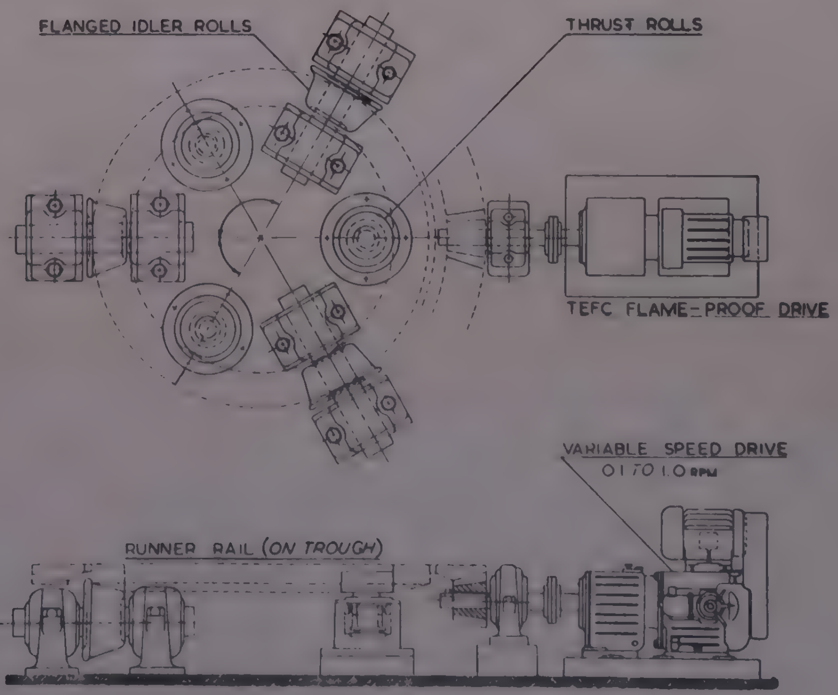

EXHAUST MANIFOLD
1070 ⌀
THERMO-WELL
ROTARY SEAL FOR FEEDER SHAFT
800
SUPPORT BRACKET

2 *Feeder-cum-exhaust section.*


1270 ⌀
6MM SHELL
SIGHT HOLE
LINING SUPPORT
1070 ⌀
1080
THERMOWELL
IGNITOR PORT
SCRAPER
1320
GAS PORT
475
SUBMERGED IN TROUGH

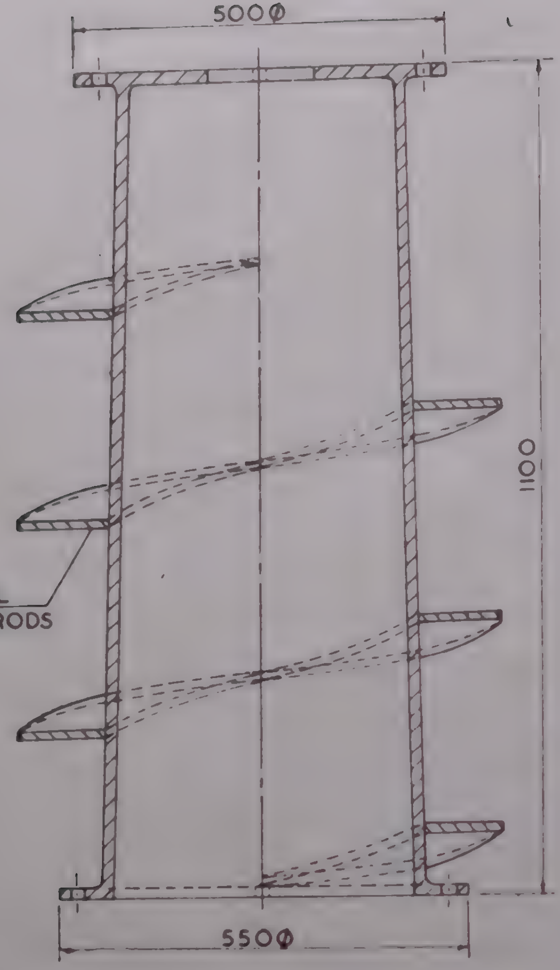

1830 ⌀
915
CAST STEEL TROUGH
STEEL SPIRAL
BEVEL RACK
1235 ⌀
ROTARY SEAL
WEAR-RESISTANT RUNNER RAIL

4 *Rotating trough with elevating spiral.*

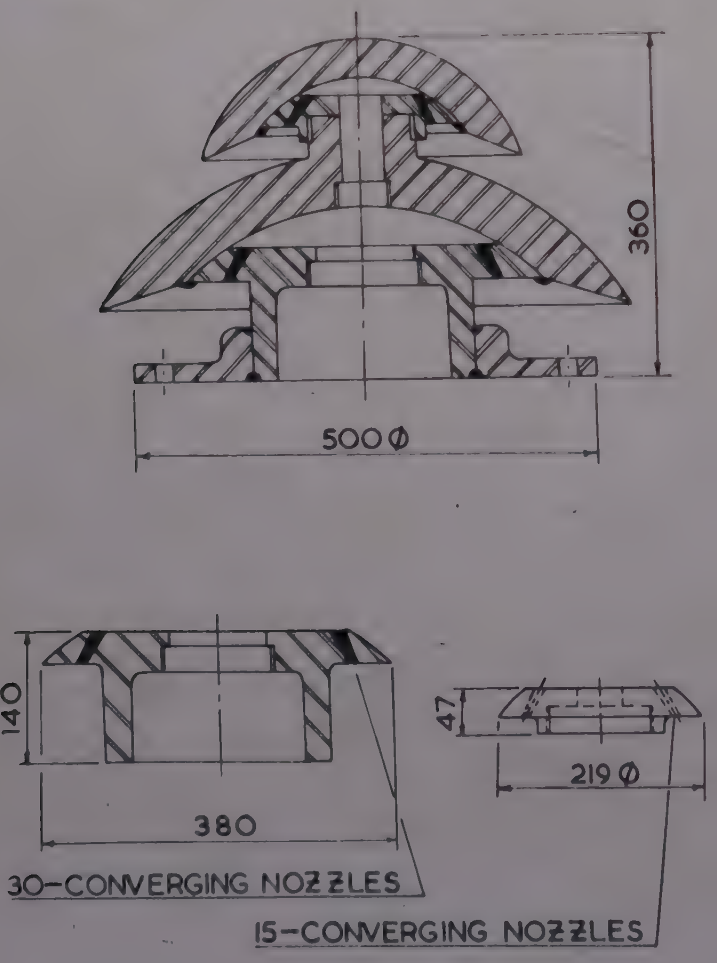

FLANGED IDLER ROLLS
THRUST ROLLS
TEFC FLAME-PROOF DRIVE
VARIABLE SPEED DRIVE
0.1 TO 1.0 RPM
RUNNER RAIL (ON TROUGH)

3 *Main stationary column.*

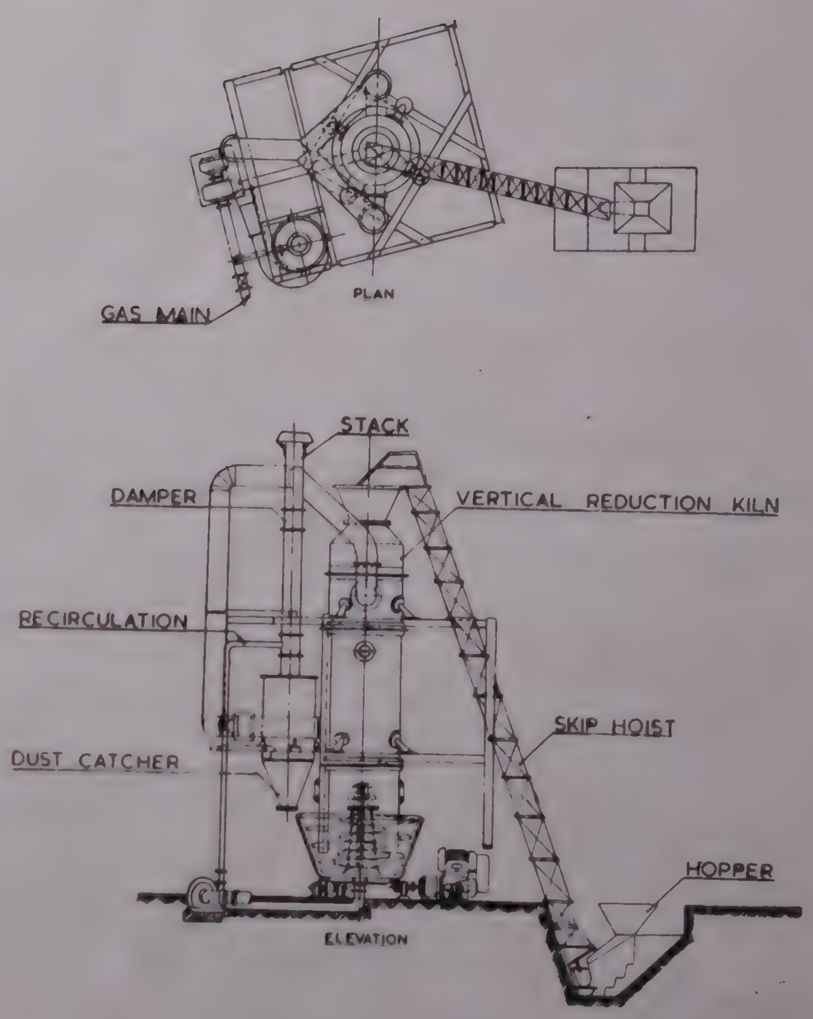
5 *Kiln drive.*


500Ø
1100
STEEL SPIRAL
OR A HELIX OF RODS
550Ø

6 *Gas distributor pedestal.*


360
500Ø
140
47
219Ø
380
30-CONVERGING NOZZLES
15-CONVERGING NOZZLES

7 *Distributor head.*


GAS MAIN
PLAN
STACK
DAMPER
VERTICAL REDUCTION KILN
RECIRCULATION
SKIP HOIST
DUST CATCHER
HOPPER
ELEVATION

8 *General assembly with dust catcher and recirculation.*

valves also permit operation of the kiln at any desired pressure gradient by maintenance of suitable top pressures. The actual residence time of materials in the reaction zone is controlled to suit process parameters by speed variation of the trough drive.

The kiln

The kiln (Fig. 1) consists essentially of a stationary mild steel shell approximately one metre in diameter and four and a half metres tall split up into three bolted sections. The lower end of this stationary assembly dips into a water filled rotating trough which serves as water seal and elevator for the wet processed material. A hopper section and a rotary feeder section form the top of the stationary column assembly. The rotary feeder is driven by a variable speed drive for control of feed rates.

At the feeder section (Fig. 2) the gas exhaust manifold has been located as an exit for spent gases from the kiln to the stack or scrubber. The main stationary column section (Fig. 3) has been provided with a sight hole and seven thermowells in two oppositely aligned rows. The end section of the stationary column (Fig. 4) which dips into the water filled trough has also been provided with a pair of thermowells, a trio of circumferentially located elliptical emergency gas feed ports and an ignitor port with a seal cap. A bevelled scraper blade is fixed to this section at the trough lip level for directing the elevated processed ore onto a launder or other conveyor. The water-filled rotating trough (Fig. 5), into which the lower end of the stationary column dips, is a 1 830 × 1 220 × 915 mm high conical steel casting or suitably protected mild steel weldment equipped with a wear resistant runner rail welded to the bottom. The trough rests upon three sets of conical idler rolls (Fig. 6) on its runner rail.

A circular bevel rack bolted also to the trough bottom is driven by a pinion attached to a vari-speed drive which serves to rotate the trough upon the idlers. An elevating spiral tack welded to the inside of the trough raises processed materials to the surface of the water seal. Gas is fed into the column via a cast iron or steel gas distributor on a hollow pedestal bolted to the base of the rotating trough (Figs. 7 and 8). A rotary seal connection at the trough base is connected to the gas main. The gas is distributed uniformly as it issues radially from 45 nozzles located along the circumference of the two tiered distributor head. The rotation of the distributor along with the trough serves to minimize chanelling and bed hanging. Limiting gas velocities are carefully controlled to further prevent bed hanging.

The gas distributor pedestal is also provided with a depressing spiral opposed to the elevating spiral across the annular space but separated by the dipping shell section. The net effect of the two spirals is that the depressing spiral pushes material down from the stationary column to the trough bottom thus effectively breaking up any tendency of the wet material to agglomerate and choke the annular space. The elevating spiral on the other hand, being located on the outer side of the stationary dipped column section, effectively lifts the material to the lip of the trough where the perforated scraper blade propels it onwards into a launder or conveyor. The arrangement works positively and without interruption for maintenance or mechanical breakdown.

Ancillaries

A recirculation system (Fig. 9) has been built into the kiln. It consists of a cyclonic type of dust catcher via which exhaust gases may be re-circulated in desired proportions by bleeding into the main gas supply line through a mixing injector. Unwanted excess spent gas is routed through the exhaust line to the stack and let off into the atmosphere either directly or via the dust-catcher to reduce atmospheric pollution. A blower cum booster in the gas line permits full control of gas inlet pressures. Butterfly valves and the stack damper also enable a build-up of top pressure in the column for higher operating pressures. An integrated support-cum-operating platform structure holds the stationary vertical column and ancillaries.

General features

Non-galling nuts and bolts, threaded unions, etc. have been specified all over to facilitate maintenance and dismantling for modification or inspection. All welding should be stress relieved.

Acknowledgement

The author expresses his grateful thanks to Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, for his keen interest in engineering design and permission to publish the paper. The author also appreciates the painstaking drafting undertaken by the staff of the Design and Engineering Division in connection with this project.

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otes and news

HOME NEWS

Thirty million tons export of iron ore by 1972

India's export of iron ore is likely to reach 20 million tons by 1966, twice the present quantity, as a result of various measures being taken to improve rail transportation and mechanisation of ore handling facilities at the ports. The Government of India has drawn up an integrated programme for achieving an export target of iron ore of 25 to 30 million tons by 1972. The programme envisages the execution of a well co-ordinated plan of production, movement of the ore from the mines to the ports and mechanisation of the ore handling facilities. It is learnt that a high level Co-ordinating Committee has been set up with the Chairman of the Minerals and Metals Trading Corporation as the convener to speed up the development activities.

Japan is India's principal buyer of iron ore and is expected to take about 6 million tons a year on a long-term basis. A number of other East European countries are also showing increasing interest in India's iron ore.

Amrita Bazar Patrika, 4.7.1964.

1·5 lakh tonnes of foundry grade pig iron to be imported every year

The Union Government is considering the import of 1 50 000 tonnes of foundry grade pig iron every year during the next three years. The step is to meet the increased demand for pig iron and the shortage caused by the delay in setting up of the Bokaro steel plant and the poor progress in the implementation of licences granted to the private sector units. The import of 1 50 000 tonnes has already been included in the Indo-Soviet trade agreement for 1964.

Hindusthan Standard, 19.7.1964.

India's steel output shows over 300% rise in 13 years

Steel production in India has shot up from 1 610 000 short tons in 1950 to 6 250 000 short tons in 1963, an increase of more than 300 per cent, according to a survey made by the International Chamber of Commerce. India is among the first six nations which have registered a rise of 300 per cent or more in steel production. Japan tops the list with a rise of 551 per cent. Next comes Mexico with 387 per cent. Rumanias' production of steel is higher by 366 per cent, the Netherlands' 364 per cent and Italy's 329 per cent. In the group of countries which registered a rise of 200 per cent to 30 per cent are : South Africa, Yugoslavia, East Germany, Brazil, Poland, Australia and Austria. The Soviet Union tops the list of the countries which have registered a rise in production from 100 per cent to 200 per cent. Others in this group are : Spain, Sweden, Czechoslovakia, Canada, Hungary and West Germany. The U.S.A. comes in the group of less than 100 per cent increase. Others in the group include Belgium, Luxembourgh, the U.K. and France. The world's steel capacity is being boosted by new production techniques that are beginning to revolutionise steelmaking operations. Since all the new techniques offer substantial cost savings, they are being eagerly adopted in the major producing countries.

Economic Times, 20.7.1964.

Full expansion of Bhilai by 1965

The entire expansion programme of the Soviet aided Bhilai steel works to raise its output from 1 million to 2·5 million tons is expected to be completed by the end of next year. The programme will cost Rs 170 crores and result in a production of 2·29 million tons of pig iron, 1·072 million tons of steel ingots and 1·1 million tons of finished steel by 1965–66. During the current financial year, about 1 07 000 tons of equipment, refractories and structurals valued at Rs 27·30 crores would arrive from the USSR. To meet the requirement of iron ore for the expansion of Bhilai, the Government is planning to develop Rajhara to 4 million tons per annum by 1965 and to prepare a scheme to work the Jharandalli mines as semi-mechanised mines to the extent of 1·5 million tons.

The Government is also considering the proposal that the Bhilai Steel Plant should undertake the production of about 20 0000 tons of special and alloy steels. The items of special and alloy steels to be produced would include welding electrode quality billets, high tensile steel billets for ACSR core wire, silico-manganese spring steel and free cutting steel billets. The designing bureau at Bhilai has prepared independently a detailed project report for the construction of the sixth blast furnace complex. The construction of this complex will start during the current Plan. A part of the equipment for this complex will be made completely at the heavy machine building plant at Ranchi.

The Sunday Standard, 19.7.1964.

Foreign collaboration for ferro-chrome units

The Metal Corporation proposes to enter into a collaboration agreement with Showa Denko Kaisha of Japan for the production of 15 000 tons of ferro-chrome. Its draft collaboration agreement is now under the consideration of the Government. Koyana Ferro-Alloys, also of Bombay, is negotiating with Birrlee of Britain for the supply of plant and equipment. Another firm, Electro-metallurgical Works of Bombay, has been licensed for the production of 10 000 tons of low-carbon ferro-chrome, for which foreign collaboration is yet to be obtained.

Iron and Steel Review 8 (1) 1964, 28.

Rs 75 crores recommended for raising zinc and lead production in Fourth Plan

The Planning Commission's Group on Non-ferrous Metals is understood to have recommended the creation of additional production capacity of 175 000 tons of zinc and 134 000 tons of lead during the Fourth Plan period at an estimated outlay of Rs 75 crores. Of this the foreign exchange component will be of the order of Rs 20 crores, as about 50 per cent of the machinery and equipment is proposed to be fabricated indigenously. The Group has also recommended that during the Fourth Plan period the capacity of the zinc smelter at Udaipur should be increased from 18 000 tons to 50 000 tons per annum if sufficient ore reserves are provided. Similarly, the capacity of the Cominco-Binani unit should be increased to 50 000 tons if continued supply of imported concentrates could be assured. The Group has suggested the setting up of one more unit based on imported concentrates with a capacity of 50 000 tons. The plant should preferably be installed at a port with a fertilizer plant to utilise sulphur from concentrates, assuming roasting is done on the plant side itself.

As regards lead, a capacity of 23 000 tons has already been licensed. The Group wants the Government to take immediate steps to increase the capacity to about 50 000 tons, if possible, on further imported concentrates. But as most of the production of zinc and lead will continue to be based on imported concentrates, the Planning Group in its interim report has stressed the need for vigorously exploiting the possibility of substituting aluminium in place of zinc or lead. It has recommended that in paints manufacture, use of alternative materials in place of zinc should be encouraged. In the case of lead also every effort should be made to reduce the demand by using substitutes.

Economic Times, 15.7.1964.

Rs 3-crore project for refractories

A Rs 2·82-crore project for refractories in the area around Chanchi Road Railway Station near Hazaribagh is being established in collaboration with West Germany and U.K. The project envisages the manufacture of 32 000 tonnes of refractories a year from locally available raw materials.

Iron and Steel Review, 8(1), 1964, 28.

NCDC plans to produce pig iron

The National Coal Development Corporation is exploring the possibility of establishing a coal-based industrial complex at Rambagh in Hazaribagh (Bihar) which will include setting up of a set of low-shaft furnaces for the production of pig iron.

Eastern Metals Review, July 6, 1964.

OVERSEAS DIARY

Research in ironmaking

The British Iron and Steel Research Association is to build a Research and Pilot Plant Laboratory Centre for ironmaking near Middlesbrough, close to the works of Dorman Long (Steel). In this centre, in addition to fundamental research, a wide range of experiments will be carried out on a sufficiently large scale to test the technological and economic feasibility of new developments. The close proximity to Teeside will make it possible to bring ore from any part of the world to the new stock yard, which will hold 10 000 or more tons. The ore can then be passed through large scale crushing, screening and materials handling operations up to a rate of 200 tons per hour. Facilities will also be available for drawing up to 10 tons of molten iron or slag at a time from the blast furnaces at Dorman Long's Clay Lane Work. In the last fifteen years, the coke required for ironmaking has fallen dramatically. Much of this is due to the work of BISRA's Iron Making Division on techniques of sintering, pelletizing, etc. BISRA has stimulated operators by providing test data, performance predictions and knowledge of foreign operation. Ironmaking represents approximately half the basic cost of making steel so that any reductions in the costs of ironmaking are important. The new centre will bring together the existing Normanby laboratory and neighbouring pilot plant premises, together with the laboratories at present operated at London's Imperial College of Science and Technology.

Financial Times, 29.4.64.

Iron ore of highest mineral content in Greece

Deposits of iron and manganese ore, which are claimed to have the highest mineral content in the world are said to have been found by a team of Soviet scientists headed by Mr Yuri Genishardy on the Volacanic Santorian Island in the Southern Aegean Sea.

Iron and Steel Review, 7(12), 1964, 40.

Record iron foundry output expected

Britain's 1 400 iron foundries are turning out castings for big manufacturing customers at such a high rate that the industry confidently expects a record output this year. Among those keeping foundries fully occupied with a steady flow of orders are the motor, construction, farm machinery, steel and general engineering industries. The Iron and Steel Board announced that castings production in the first quarter production represents a 6·5 per cent improvement on the previous quarter and was 18 per cent up on the first three months last year.

Financial Times, 23.5.1964

Spain to have second blast furnace

A big boost to Spain's steelmaking capacity will result with the completion of a new blast furnace at Avilès for which Bethleham Steel Company is furnishing a giant hard-surfaced cast steel bell and hopper assembly.

Under construction by Kopper Co. Inc. of Pittsburgh, for Empresa Nacional Siderugica, S.A., of Madrid, the furnace is expected to produce 2 000 metric tons of pig iron daily, thus becoming Spain's largest producer. The new furnace, the second to be designed by Koppers for the Spanish steel firm, will have a hearth diameter of 28 ft and will represent the most advanced blast furnace technology. It will be equipped for high pressure operation, with a maximum top pressure of 15 pounds per square inch. As shipped, the bell weighed 70 000 pounds, the hopper ring 22 000 pounds, and the four hopper segments 13 000 pounds each. Diameter of the bell at the lip was 16 ft 6 in. It stood 10 ft 6 in high. Wall thickness varied from six inches at the bottom to three inches at the dome.

Blast Furnace and Steel Plant 52 (3) 1964, 271

Three-bell operation reported by Fuji

The Fuji Iron and Steel Co. has reported successful operation of a three-bell pressure top on a blast furnace at the Muroran Works. The new system was blown in January of 1963 on the No. 3 furnace, and went into high pressure operation four months later. After another four-month test run period, it went into commercial production. Pig iron output of the furnace averages 1 800 tons per day as against 1 200 tons per day for the other furnaces. Pig iron output per furnace inner volume increased to 1·83 as against an average of 1·3. The

No. 3 blast furnace at Muroran, for example, can turn out anywhere from 1 200 to 1 800 tons per day, depending upon the pressure control. As a result, the plant can reduce or expand its pig iron output to keep production in line with demand,

Iron and Steel Engineer, XLI (3) 1964, 203-204.

Plan to step up steel output

The Executive Committee of the Association of Yugoslav Foundries have adopted a plan to increase output of crude steel in Yugoslavia to a total of 1 700 000 tons this year. which is 100 000 tons more than in 1963 and production of pig iron to a total of 1 100 000 tons. Increases in the steel products output have also been planned by the Association.

Iron and Steel Review 7 (12) 1964, 40.

Computer controlled machine tool

A completely computer-controlled machine tool capable of several different operations is to be shown for the first time at the forthcoming Machine Tool Exhibition at Olympia by Stavely Industries. It is the result of two years of development, with the help of a grant of £3 30 000 from the Department of Scientific and Industrial Research. The construction was done by the subsidiary, James Archdale and Co. The machine is designed to carry out all operations—drilling, milling, reaming and so on—in one set-up. It can be worked under the normal manual control or full computer control, with variations between the two. The tool is designed to cut materials ranging from light alloys to die steel and can take work pieces up to 4 feet cube. Accuracy is within 0·003 inch. The spindle is powered by a variable speed hydraulic drive. The research started at Stavely Industries in 1959, but the project was seen to be very expensive. Following a survey by the D.S.I.R. of the machine-tool industry in the U.K. the Department was given powers to make grants to machine-tool manufacturers. The first stage of the grant-aided research is the prototype to be shown at Olympia.

The Financial Times, 18.6.1964

Recent developments

Improved coatings protect steel tanks from acid

Two new coating systems have been developed by Ceilcote Co., Cleveland, Ohio to protect industrial plating and storage tanks from attack by water, alkalis and acids. The first, a laminated glass fibre and filled bisphenol polyester resin system provides an exceptionally hard, tightly bonded liner in steel tanks. The cured coating resists dilute mineral acids and alkalis, most salts and organic chemicals at temperatures up to 160°F. Applied 1/8 in thick, the lining is also claimed to be especially effective for protecting steel from attack by concentrated acids, such as hydrochloric and phosphoric which are found in pickling and plating processes.

The second coating system is a cement comprised of aluminium-silicate powders and special additives to improve adhesion and dispersion. Designated 'Pre-Krete Formula G 8', the cement is intended for application on new or old steel. It imparts good resistance to attack by many acids, such as dilute lactic and hydrochloric, tannic and other dilute organic acids. Because the coating has the same coefficient of thermal expansion as steel, it is unaffected by temperatures ranging to 1 000°F. The cement comes bagged as a dry powder, which forms a trowelable lining material after mixing with water. It can be applied over any steel surface, wire finishing is the only preparation necessary. The coating cures in 24 hr or less, depending on humidity. After curing for 3 days, the lining has a compressive strength of 11 000 psi and tensile strength of 1 400 psi. Since the coating also exhibits high resistance to abrasion, it has been used on ash hoppers, dust collectors, coal hoppers, gas scrubbers and grain chutes. In typical applications material cost of the lining is about 60 cent per sq ft.

Materials in Design Engineering 59 (3) 1964, 169-170

Swedish welding technique

A development by the ESAB welding organisation is already in operation in Swedish plants in a unit which automatically welds condenser or refrigeration tubes in large or small stacks. The method has proved to be highly efficient and laboursaving and has an application in such fields as ship-building, refrigeration, chemical, oil, nuclear and general engineering. The unit, which is slung from a gantry or crane, is fitted in turn on to the top of each individual pipe which has to be welded to the end supporting plate or tray. For this purpose a special mouth piece for the tube diameter is supplied. This tube or guide is rotated by a motor at the required welding speed. The guide is spring loaded so that if rotation stops due to obstruction, no damage is done to the drive motor and gearbox. Welding is carried out under a gas shield of CO_2 and the electrode used is ESAB's OK Autrod 51, in 20 or 18 swg diameter. A special adjusting clamp, which carries these supplies allows the electrode tip to be set at the correct angle in the joint. Welds can be carried out on tubes with an internal diameter as small as 13/32 in and up to a maximum of 3·93 in.

Iron and Steel 37 (4) 1964, 163

Roll facing technique

A new development in wear resistance surfaces for rolls which offers important economics to manufacturers and users of papermaking and printing machinery, plastics and rubber milling equipment is announced by Brookes (Oldbury) Ltd., a T.I. engineering division company. The new process, representing an ingenious advance in centrifugal casting, involves the metallurgical bonding to roll surfaces of a layer of 'Xaloy 306', a complex nickel-cobalt alloy with additions of chromium, silicon, carbon and boron, which offers outstanding resistance to abrasion and corrosion. For over 25 years this material, available hitherto only as an internal lining in cylinders and pipes, has given remarkable service in plastics extruders and injection moulding machines, and pumps dealing with difficult materials like crude petroleum.

As an external roll surface, 'Xaloy 306' has several important advantages. The wear surface, usually more than 1/16 in thick, has a consistent hardness throughout its depth of about 50 Rockwell C, which is maintained at temperatures up to 1 000°F (540°C). Corrosion and abrasion resistance are inherent in the material and not dependent on heat treatment of surface processing. A low coefficient of friction and a high degree of impermeability discourage pick-up and contamination of the rolls or the product; the surface can be highly polished to a 2 micro-inch finish if required. It exhibits extreme resistance to a wide range of corrosive products, including sulphuric and hydrochloric acids.

The depth of the alloy layer, some 20 or 30 times thicker than a typical chrome plate, in combination with a coefficient of thermal expansion very close to that of the best steel, completely eliminates the cracking or worming. Should wear or damage eventually occur, reworking involves only a simple regrinding and polishing operation instead of costly and time consuming stripping and replating.

The new rolls available in diameters up to 18 in have been introduced after extensive field testing which included the actual processing of asbestos filled vinyle, high pressure polyethylene, synthetic rubbers and other abrasive, corrosive or tacky materials.

Metallurgia 69 (414) 1964, 190.

Alum-a-lead

A new mouldable aluminium compound—said to provide a superior, yet economical, metallic repair material for automotive body work, has been developed by Ditzler Color Division of Pittsburgh Plate Glass Company. Called 'Alum-A-Lead', it consists of a newly developed liquid binder and specially treated Alcoa aluminium flake. Easily applied to sanded steel or alumium with a squeegee or spreader, it is produced by mixing the liquid resin with the activated aluminium powder. This forms a self-curing solid aluminium material that is easily moulded for repairing or restoring the contours of metal on today's automobiles.

Superior to traditional solder because it can be used on areas where heating the metal is not practical—such as ground glass, rubber and synthetic auto-top materials—practical tests show it is also much more economical to use than solder. It is said to spread further, and smooth and level off more easily. It featheredges to a smooth fine edge that will neither show nor chip off. It demonstrates outstanding adhesion and durability since it, does not absorb moisture. It resists formation of rusts under the film or creeping under the edge. Since no heat is required in application, warping of large flat areas of metal is averted.

Curing time is very rapid and may be adjusted to climatic conditions. It accepts any standard synthetic or lacquer primer, or primer surfacer, followed by the finish colour. Hold out of top coats is excellent, eliminating flat spots.

Light Metal Age, 22 (182) 1964, 5.

Hi-speed vacuum furnace

A new 2 400°F (1 316°) furnace equipped with a unique cooling bung permitting accelerated cooling rates has been announced by Ipsen Industries, Inc. The new furnace is a standard Ipsen VFC-224 cold wall unit designed especially for high-speed, stainless and tool steel heat treatment such as bright hardening, sintering, annealing, stress relieving and normalising.

The cooling bung is located between the circulating fan and the charge. Upon completion of the heat cycle the vessel is loaded with inert gas, a cylinder opens the cooling door and the fan is energised, beginning the cooling cycle. The open bung allows coolant gas to be blasted directly through the load permitting fast cooling to below critical temperatures. Increased circulation permits cooling of the charge from 2 250°–1 000°F in less than two minutes.

The VFC-224 has a charge area 15 in wide × 24 in deep × 10 in high. Maximum operating temperature is 2 400°F at an ultimate vacuum of 0·01 micron Hg. Heating elements surround the load providing and cycle control is fully automatic. All that is necessary is to set the soak timers and press the start button. Recording controllers programme preheat and high heat temperatures, the degree of vacuum and partial pressures of inert gas, such as nitrogen or argon. Vacuum, gas or fan cooling modes are present with a selector switch. Should vessel pressure rise above the present level, the Ipsen Vacutronik shuts off the heating elements. A panel light signals completion of the automatic cycle.

Metallurgia 69 (414) 1964, 191.

A new hydraulic cold extrusion press

A new hydraulic cold extrusion press capable of a variety of forward, backward, or combination extrusions has been developed by E. W. Bliss (England) Ltd., in collaboration with the Production Engineering Research Association of Great Britain. Being hydraulic, the press is capable of uniform pressure exerted throughout the working stroke, a range of pressing speeds, and easier motion changeover for different applications. Adjustable inner and outer slides make the press suitable for different punch lengths. In forward extrusion, a mandrel is attached to the inner slide and a hollow extrusion punch to the outer slide. In backward extrusion, the punch guide and stripper are attached to the outer slide and the extrusion punch to the inner slide. A twin cylinder ejector is mounted below the press bed for removal of the component from the die. The centre post is removable to allow for longer forward extrusions. Interlocks prevent starting of the next cycle before the ejector has been returned to the bottom position. Other advantages include double acting main rams and cylinders, extra heavy press frames, and long grinding lengths to provide rigidity and accuracy.

Steel 154 (19) 1964, 71.

IMPORT OF NON-FERROUS METALS

(Metric tons)

		1959	1960	1961	1962
Aluminium	Unwrought	6 915	8 116	9 574	14 929
Aluminium	Wrought	12 401	15 370	13 728	22 202
Brass, Bronze	Unwrought	1 962	3 698	2 927	457
Brass, Bronze	Wrought	2 242	4 000	3 871	1 310
Copper	Unwrought	49 563	61 439	60 308	67 875
Copper	Wrought	1 274	1 639	1 595	2 728
Nickel, Nickel alloy	Unwrought	912	1 214	1 329	1 303
Nickel, Nickel alloy	Wrought	107	293	413	227
Lead	Unwrought	24 059	24 830	24 381	34 941
Lead	Wrought	97	173	404	149
Tin	Unwrought	4 465	3 903	4 630	4 640
Zinc	Unwrought	48 561	66 914	73 144	76 919
Zinc	Wrought	262	1 337	900	1 400
Aluminium	Conductors	4 584	3 868	2 081	238
Copper	Conductors	337	87	183	965
Winding wires		874	735	1	4
Antimony		82	21	0·88	—
Non-ferrous alloys	Unwrought	1 797	2 928	1 879	2 182

Source : Eastern Metals Review, Annual Number, 1964, 72.

EXPORT OF NON-FERROUS ORES AND CONCENTRATES

(Metric tons)

	1959	1960	1961	1962
Bauxite	23 560	75 641	99 721	175 621
Chromite	81 651	41 196	41 843	16 534
Ilmenite	281 057	228 916	125 213	103 245
Manganese ore	985 651	1 160 201	1 613 592	782 689
Zinc	12 616	9 301	10 196	10 751

Source : Eastern Metals Review, Annual Number, 1964, 73.

MONTHLY AVERAGE PRICES OF PRINCIPAL NON-FERROUS METALS IN INDIA DURING THE YEAR 1963

(In Rupees per quintal)

	Jan.	Feb.	March	April	May	June	July	August	Sep.	Oct.	Nov.	Dec.	Year
Bombay													
Copper scrap (utensil)	537·70	551·36	558·41	571·14	579·50	582·17	576·78	577·47	579·73	584·81	590·86	608·62	574·88
Virgin lead	163·26	172·27	181·36	189·59	202·38	205·00	203·52	200·47	204·55	211·17	221·10	217·12	197·65
Tin	3013·48	3014·54	3054·55	3178·64	3654·62	3985·42	3798·52	3365·29	3430·94	3403·04	3300·95	3190·83	3365·90
Electro-zinc	243·22	257·36	272·86	264·32	262·46	261·25	260·00	255·94	256·28	250·96	250·38	250·92	257·19
Calcutta													
Copper scrap (utensil)	545·98	559·60	558·42	568·50	565·45	565·54	571·17	573·54	581·18	583·64	588·91	610·90	572·99
Virgin lead	154·36	169·77	175·13	184·24	193·00	200·00	206·48	208·32	209·92	210·00	212·87	215·00	194·92
Tin	3054·54	3075·45	3065·21	3160·60	3683·33	3918·20	3752·04	3327·60	3426·28	3344·55	3219·13	3219·17	3353·92
Electro-zinc	258·09	286·77	284·42	274·64	265·59	260·40	258·52	251·48	254·71	266·27	267·78	269·17	266·49

Source : The Eastern Metals Review, Annual Number, 1964, 184.

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Research In Standardization

'STANDARDIZATION' has been defined as the 'process of formulating and applying rules for an orderly approach to specific activity for the benefit and with the co-operation of all concerned and in particular for the promotion of optimum overall economy taking due account of functional co-ordination and safety requirements'. The role of research in such a definition of standardization on the face of it appears somewhat obtrusive but on rational analysis and study it would emerge as a vital guiding and dominating factor.

In the context of industrial development in India in our successive Five Year Plans, the need for an all-out effort for standardization of metals and metal products in the different fields of ferrous and non-ferrous metal industry became imperative. It is in these fields of standardization that the National Metallurgical Laboratory has been playing an increasingly vital role at all stages of the formulation of draft standards, their finalisation and at a later stage in the revision of the existing standards.

The National Metallurgical Laboratory apart from acting in an advisory capacity has undertaken comprehensive research programmes and investigations for the Indian Standards Institution to formulate the technical know-how, process evaluation, metallurgical characteristics and physical properties of finished products. Illustrative of such research contributions of NML in these fields would be the formulation of standard foundry sands for testing ; methods of physical tests for foundry sands ; test methods and parameters for foundry bonding materials ; standardization in the field of testing of corrosion resistance materials ; standardization in the field of testing of metals and alloys ; standardization in the field of refractories ; standardization in the field of chemical analysis, etc.

The importance and scope of research in the field of standardization are today recognized to be indispensable and were adequately highlighted at the International Organisation for Standards at their Sixth Triennial General Assembly which was held at New Delhi from 8th to 21st November, 1964.

Production of Low Residual and Soft Iron

R. D. Gupta
P. K. Gupte
B. R. Nijhawan

Research and development work have been undertaken at the National Metallurgical Laboratory to produce low residual iron for use as the basic raw material in the manufacture of special irons, alloy steels and super alloys, and also for use as soft magnetic material. Specialised refining technique has been developed at the National Metallurgical Laboratory for the production of low residual iron employing mild steel scrap as the main raw material, conforming to composition range of C%–0·03 max. S%–0·01–0·02; P%–0·004-0·018 : Si%–0·01–0·12 ; Mn% trace–0·11 and Al% trace–0·21.

LOW residual iron i.e. iron with exceedingly low carbon, sulphur, phosphorus, silicon and manganese contents forms the basic charge in the production of special alloys such as permanent magnet alloys, heat resistant alloys, super alloys etc. in which the presence of even minute impurities is highly undesirable. Such iron has not so far been produced in India on any organised scale and entire requirements thereof for the industry are met by imports of Armco, and identical pure low residual irons.

The process for the manufacture of low residual iron is somewhat closely guarded. Sokolov et al[1] have reported the manufacture of Armco soft iron by the basic open hearth process with a nominal composition of carbon 0·025%, silicon 0·05% ,manganese 0·05%, sulphur–0·025%, phosphorus–0·015, chromium–0·10% nickel–0·20% and copper–0·25%. They attempted to further lower the carbon, sulphur and phosphorous contents by blowing oxygen and compressed air and obtained a product containing carbon-0·014%, silicon-trace, manganese-0·018%, sulphur-0·015%, phosphorus 0·007%, chromium-trace, nickel-0·14%, copper-0·15%.

Intensive research and development work have been undertaken at the National Metallurgical Laboratory on the production of low residual iron in basic electric arc furnace attaining very low carbon, sulphur, phosphorus, silicon and manganese contents in the finished product for use as soft magnets and in the production of special substitute alloys under development at the National Metallurgical Laboratory. The work was extended to produce the pure iron in the form of shots of optimum size. The raw material used in this research and development work was unsorted plain carbon steel scrap.

Experimental work and results

Initial small scale trials were made in a 25 kg magnesite line direct arc electric furnace with manual control of arcing and power input. A double slag (oxidising and reducing) melting technique was employed, with the diference that two oxidising slags (instead of one) were made to obtain a low phosphorus content, less than 0·01% and low carbon content less than 0·03%. To achieve this, iron ore additions were made to the melt which was suitably oxygen lanced. After removing the second oxidising slag, the reducing slag was made with lime, fluorspar and aluminium. The melt was then cast into ingot moulds. The carbon content of melt was less than 0·045%.

Carbon cotent of the melt could further be reduced with automatic electrode control since in manual control it is difficult to maintain the arc without the electrodes impinging on the melt causing carbon pickup thereby. Full scale melting trials were made in an 800 kg electric arc furnace (Brown Boveri) operated from a 450 kVA transformer having six different voltage tappings namely of 73, 80, 88, 98, 111 and 127 volts. The initial charge of of unsorted plain carbon steel scrap was so adjusetd as to give an opening carbon of about 0·3%. Requisite quantity of limestone was charged along with the scrap. Iron ore was added to initiate the 'boil' during scrap melting period in order to facilitate elemination of phosphorus which would otherwise be retarded by subsepuent high melt refining temperatures, particularly during oxygen lancing. The first oxidising slag was taken out immediately after the scrap melting was completed and a fresh basic and oxidising slag was made up with limestone, fluorspar and mill scale. After oxygen lancing operation, the second oxidising slag was run out. At the end of each oxidising period, bath sample was taken primarily for the determination of carbon and phosphorus contents. The duration of oxygen lancing was adjusted in relation to the carbon content of the first melt sample. In the second melt sample taken during the second oxidising period, manganese and sulphur contents were also analysed.

After removing the second oxidising slag, the bath was partially deoxidisied with ferro-silicon and a fresh reducing slag was made by the additions of limestone and fluorspar. The bath was held under this slag for about 45 minutes in order to remove sulphur. Slag and the metal were rabbled during this period. Two bath samples were taken during the reducing slag operation, the slag was thereafter run off and a fourth slag was made with limestone and flourspar alone. Immediately following this, oxygen lancing was done for a short time till all the silicon in the bath had been oxidised as judged by the fumes issuing from the furnace. As soon as this stage was reached, the bath was actively rabbled with aluminium sticks (6 kg/ton) for final deoxidation and the

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Messrs R. D. Gupta, P. K. Gupte and Dr B. R. Nijhawan, National Metallurgical Laboratory.

TABLE I Time schedule of heat No. EF77 of low residual iron carried out in 800 kg electric arc furnace.

Cast No. E.F 77		
Power on	10.50 a.m.	
Charging complete	12.45 p.m.	
Complete melt	1.15 p.m.	
I Slag off (oxidising)	1.40 p.m.	
II Slag off ,,	2.28 p.m.	
III Slag off (reducing)	3.24 p.m.	
Tapped	4.00 p.m.	
Total time taken	5.30 hr	
Basic charge		
Heavy scrap	500 kg	
M. S. pipe	200 kg	
Misc. light scrap	100 kg	
Limestone	10 kg	(with the charge)
Limestone during melting	5 kg	12.00 p.m.
Iron ore	10 kg	12.25 p.m.
Charge melted		1.15 p.m.
Bath sample I		1.30 p.m. (0·13%C, 0·032%S, 0·013%P)
Bath temperature	1550 C	(1.38 p.m.)
1st Slag off (oxidising)		1.41 p.m.
Slag making mixture :		
1. Limestone	12 kg	1.47 p.m.
2. Fluorspar	1·5 kg	
3. Mill scale	2·0 kg	
Bath sample II for C, S & P		2.21 p.m. (0.08%C, 0·03%S, 0·0038%P)
2nd Slag off (oxidising)		2.28 p.m.
Ferro silicon	4 kg	2.32 p.m.
Slag mixture :		
1. Limestone	12 kg	2.33 p.m.
2. Fluorspar	1·5 kg	
Bath sample III for C, S & P.		3.15 p.m. (0·06%C, 0·013%S, 0·012%P)
Temperature		1600°C (3.20 p.m.)
3rd Slag off (reducing)		3.24 p.m.
Slag making mixture :		
1· Limestone	12 kg	3.25 p.m.
2. Fluorspar	1 kg	
Oxygen, blown at 100 psi		3·33–3·39 (6 minutes)
Aluminium stick	5 kg	3.43 p.m.
Bath sample IV (C, S & P)		3.48 p.m. (0·03%C, 0·012%S, 0·0082% P)
Bath sample V (C, S & P)		3.55 p.m. (0·02%C, 0·012%S, 0·0063%P)
Tapped		4 p.m.

melt was tapped after about 10 minutes. The temperature of the bath was maintained at about 1600°C, the yield of the metal was approximately 80% of the initial metallic scrap charge.

Time schedule of a typical heat of low residual iron made in 800 kg electric arc furnace is given in Table I.

The procss described in Table I was modified to some extent in other melts, typical of these alterations are illustrated by Heat Nos. 78, 87 and 92.

Heat No. 78 : The process followed was the same as for Heat no EF77 as detailed in Table I except that prior to final deoxidation of the molten bath with aluminium sticks the slag cover of the bath was removed and a fresh slag was made with fluorspar and limestone.

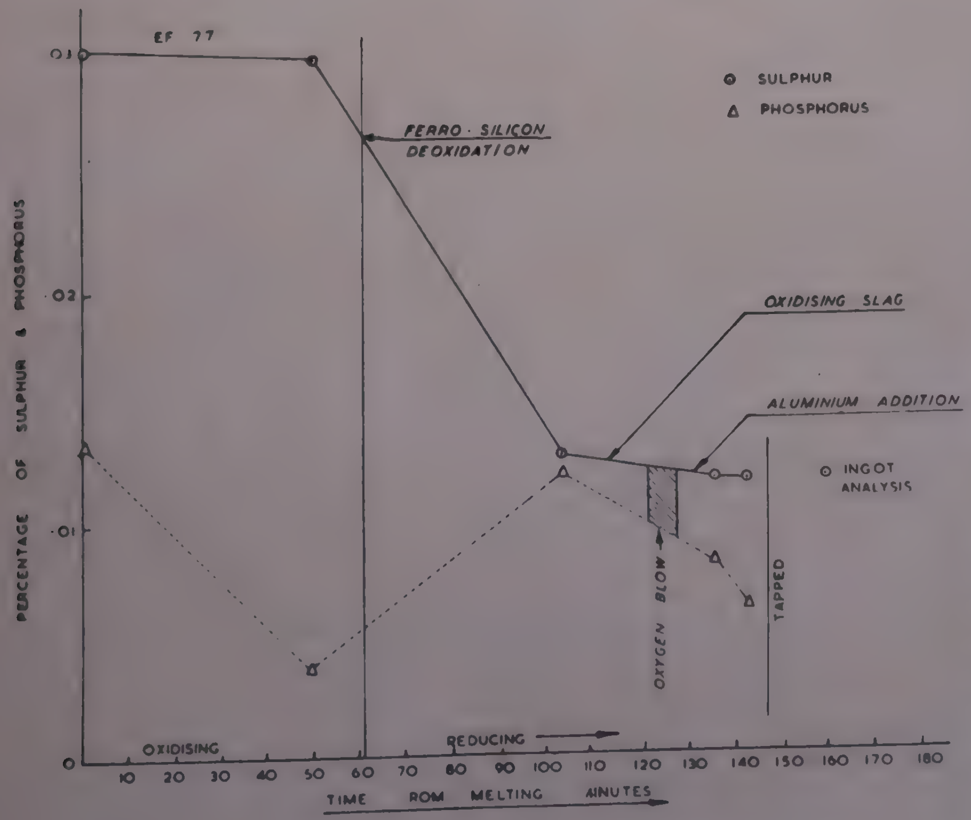
Heat No 87 : In this heat, after removing two oxidising slags, bath was deoxidised only with aluminium and no ferro-silicon was used. The usual oxygen blow after the reducing slag was abandoned.

Heat No. 92 : The procedure followed was similar to that of heat No. EF 77 except that oxygen blow was curtailed from 6 minutes to one minute only.

Chemical analyses of some of the low residual iron heats made are given in Table II.

TABLE II Chemical analyses of some low residual iron heats.

Heat No.	% Composition						
	C	Si	Mn	S	P	Al	N
E.F. 77	0·02	0·07	0·053	0·012	0·016	Tr	0·0055
E.F. 78	0·02	0·047	Tr	0·014	0·006	0·14	0·009
E.F. 83	0·01	0·03	0·05	0·02	0·0036	0·10	0·0059
E.F. 84	0·025	0·05	0·082	0·028	0·013	0·10	0·006
E.F. 87	0·02	0·01	0·04	0·02	0·004	0·10	0·0074
E.F. 92	0·03	0·12	0·04	0·0095	0·0094	0·210	0·0053
E.F. 94	0·03	0·042	0·11	0·019	0·007	Tr	0·0062



1 *Sulphur and phosphorus content of metallic bath with respect to time during the melting of heat EF 77.*

Four typical combined curves for sulphur and phosphorus are given in figures 1, 2, 3 and 4 for heats Nos. 77, 78, 92 and 84. They indicate the manner in which sulphur and phosphorus changes in the metallic bath during the process of manufacture of low residual iron.

Ingot structure

All the melts made were teemed into big end up ingot moulds of size 4½″ square. In order to determine the effects of various slagging and deoxidation treatments on ingot structure, the transverse cross sections of the ingots selected from representative melts namely EF 77, EF 78 and EF 92 were comprehensively studied. Macro-structure of these sections are given in Figs. 5 ,6 and 7. It would be seen that ingot sections for EF 77 (Fig. 5) were full of blowholes while the ingot sections for EF 78 and EF 92, which appeared sound when viewed in the polished state, showed central cracks on macroetching with nital (Figs. 6 and 7).

Forging characteristics

Ingots from heat Nos. EF 77, EF 78 and EF 92 were hot forged using a 10 cwt pneumatic hammer in the temperature range of 1150°C to 950°C. Tendency to form fish cracks over the entire surface of the ingot and finally to disintegrate was observed for ingots from heat Nos. EF 77. A small piece could however be forged with great difficulty to ¾" sq. section from the usual 4"sq. ingot section. The macrostructure of a transverse section of the forged piece is shown in Fig. 8. Ingots from Heat No. EF 78 also behaved similarly, the disintegration was somewhat more pronounced whilst ingot from Heat EF 92 could be hammer forged under similar forging conditions without any difficulty. Fig. 8 shows the structure of the forged section at three different stages during forging. It was observed that while centre porosity was visible in pieces forged down to 1½" sq. to 1⅛" sections, no porosity was observed when the section had been reduced to ¾" sq.

Casting of shots

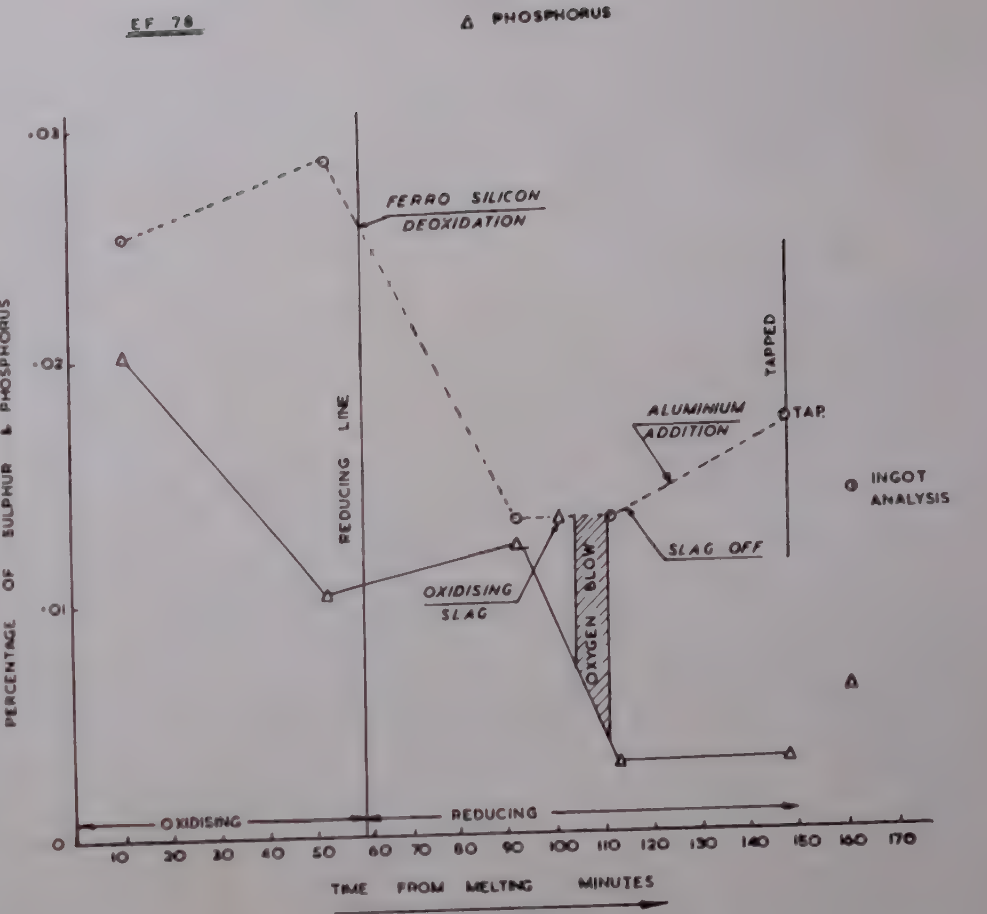
Basically such pure residual iron is used as a base charge for making special steels and super alloys. As such, for easy handling and economical charging into the electric furnace the melt was directly cast into shots of optimum size most successfully. Fig. 9 shows the size and shape of the shots thus produced at the National Metallurgical Laboratory. Fig. 10 gives a general view of the set up being employed for this purposes.

Soft magnets and test

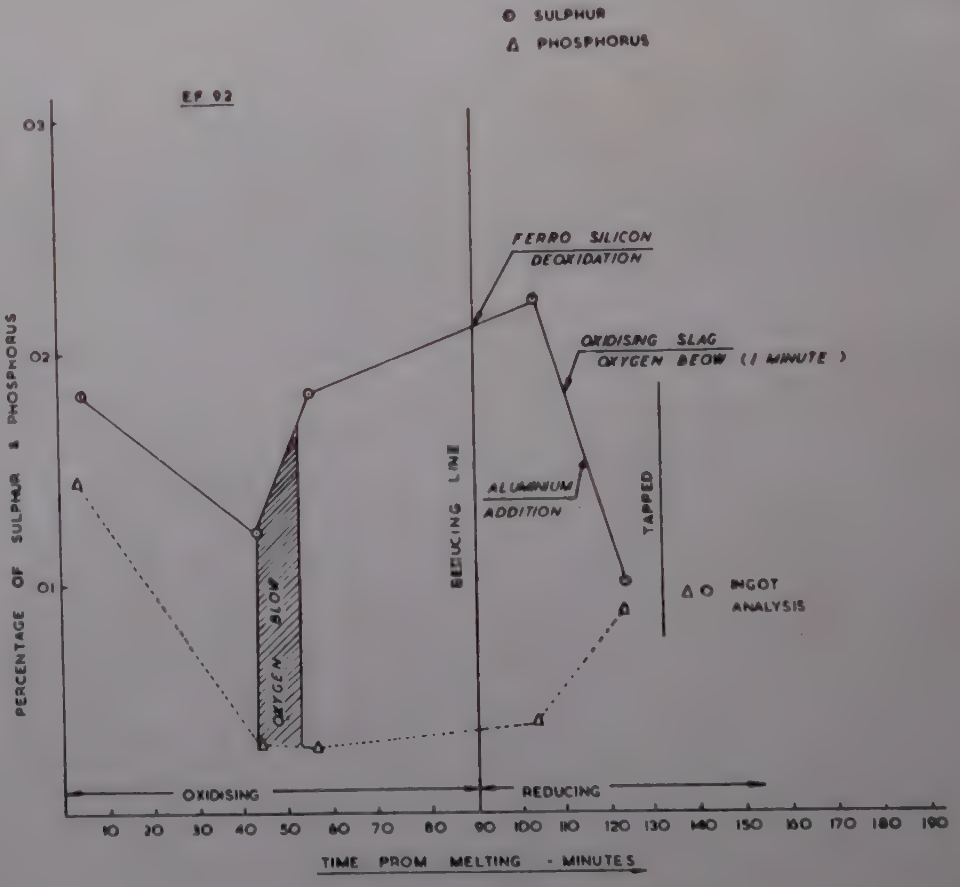
Four inch square ingots of heats EF 77 and EF 92 were forged to ¾" square bars for making test pieces for testing the magnetic behaviour of the metal. Each bar was subsequently sectioned longitudinally into four bars which were anneal-at 1 050°C. Two pieces from each bar were machined to approximately 0·1" diameter and test pieces prepared in length/diameter ratio of 70. These sambles were there after given a stress relieving treatment in a salt bath kept at 600°C and later tested ballistically for magnetic properties. The coercive force values for saturation inductions are given in Table III.

Discussion

When a normal plain carbon steel scrap containing about 0·2—0·5% carbon is used, opening carbon in the melt is about 0·2%–0·3% with a silicon content of about 0·04% and phosphorus 0·02%. Since phosphorus removal is normally facilitated at low temperatures iron ore additions are made for a good boil and later after running off this slag, a second oxidising slag is made which is followed by oxygen lancing. Oxygen lancing gives a quick rise in the melt temperature due to oxidation of residual silicon in the bath and also assist in making the second slag and bringing down the carbon content of the melt to the required low level. The iron ore additions and duration of oxygen lancing are suitably adjusted depending upon the opening carbon content.



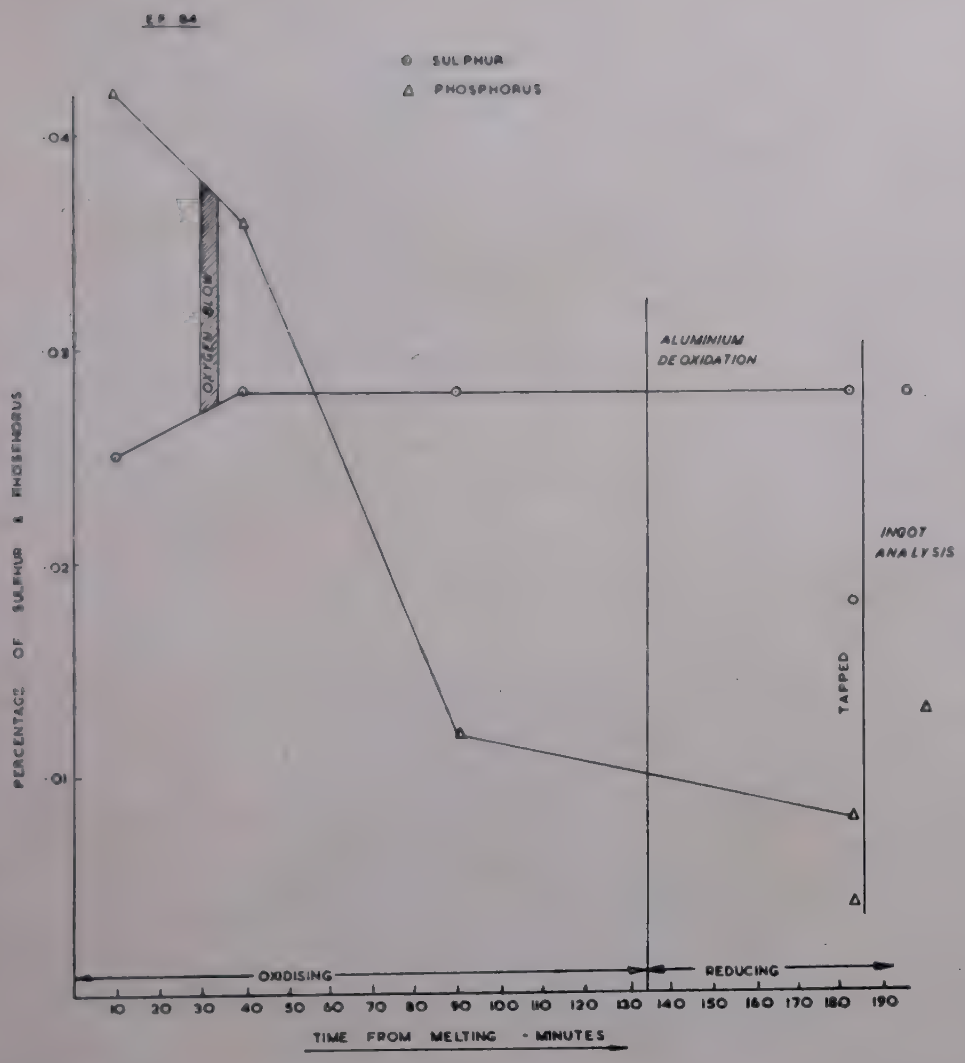
2 *Sulphur and phosphorus content of metallic bath with respect to time during the melting of heat EF 78.*



3 *Sulphur and phosphorus content of metallic bath with respect to time during the melting of heat EF 92.*

The bulk of the basic oxidising slag in an electric arc furnace normally consists of 2 to 5% of the total charge. The basicity (lime/silica ratio) of the slag ranges from 2 to 3. The FeO content varies from 5 to 25% depending upon the carbon content of the bath. The flourspar additions are required in case of slags with low FeO and high lime contents for providing a fluid working slag.

The mechanism of phosphorus removal is briefly described in the following page.[2–7]



4 *Sulphur and phosphorus content of metallic bath with respect to time during the melting of heat EF 84.*

TABLE III **Coercive force values for specimens from heat no, 77 and 9**

Sample No.	Coercive force (oersted)	Saturation induction (gausses)
EF 77	1·4	19130
EF 92	1·1	1 857

Phosphorous in the metal reacts with FeO of the bath and forms P_2O_5 (eqn. 1), which reacts with the free lime in slag and forms calcium phosphate in the following stages :

$$2P+5\ FeO \rightleftharpoons P_2O_5+5\ Fe+Heat \qquad (1)$$

$$P_2O_5+n\ CaO=(CaO)n\ .\ P_2O_5 \qquad (2)$$

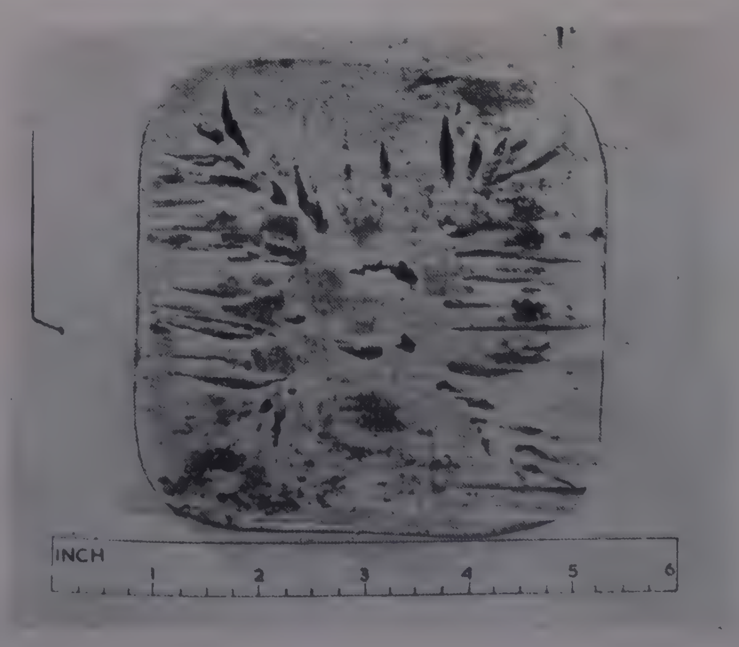
Reaction (1) indicates that for favourable dephosphorisation, the bath should be rich in iron oxide. Again the oxide content of the bath is known to vary inversely with carbon content of the melt as shown in Fig. 11.[8, 9] At melt down the low carbon steels will have sufficient FeO in the bath to lower its phosphorus content to low levels. Since FeO is soluble in the steel bath and also forms part of the slag, an equilibrium would exist in the distribution of FeO between slag and metal. High FeO content in the melt would result in a slag also rich in FeO.

Since the reaction represented by equation (1) is exothermic the formation of P_2O_5 is favoured at lower temperature. The effect of temperature on phosphorus removal is illustrated in Fig. 12,[10] where values of the logarithms of the equilibrium consistant of P in slag and liquid iron $\left(\text{the value of } kp=\frac{\text{Concentration in slag}}{\text{Concentration in steel}}\right)$ are lotted against the reciprocal of temperature $\frac{(10^4)}{T}$. The graph shows that log kp (phosphorus bearing capacity of the slag) increases with decrease in the working temperature showing that phosphorus removal is favoured at lower temperature.

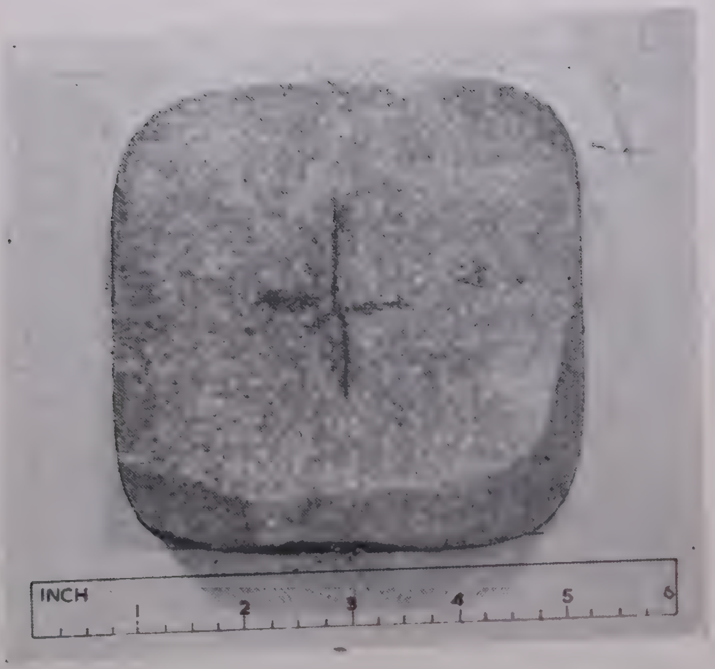
Equation (2) indicates that due to the acidic nature of P_2O_5 it reacts with the highly basic free lime to form calcium phosphate. For this reaction to proceed, it is necessary that the slag should be highly basic with adequate free lime. CaO and SiO_2 normally present in the initial oxidising slag, always combine to form dicalcium silicate which account for a CaO/SiO_2 ratio of 1·87. Thus when the CaO/SiO_2 ratio is 1·87, the slag will be neutral. For the basic slag to have excess free-lime, the CaO/SiO_2 ratio has to be more than 2.

From the foregoing, it can be concluded that for efficient dephosphorisation, the slag should have a CaO/SiO_2 ratio of more than 2 and a high FeO content. Winkler and Chipman[11, 12] have studied the effects of varying the FeO contents and basicity of slag in the basic open hearth furnace, on the resulting phosphorus content of the steel. Based on their work Derge and Tenenbaum[13] have drawn a curve (Fig. 13), which clearly shows that keeping either of the two functions (FeO content or basicity) low, any increase in either beyond optimum limits i.e. basicity 2·5 and FeO 20–25%, does not produce any appreciable reduction in the phosphorus content. It, therefore, follows that it is essential to have both the variables within optimum limits to attain very low phosphorus centent in the metal.

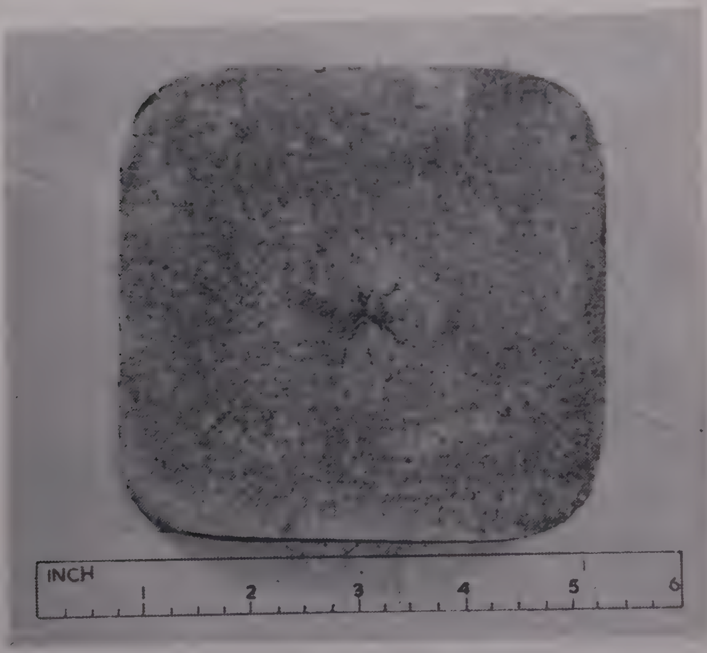
In experiments, with low carbon steel melts, the initial phosphorus obtained was of the order of 0·015% of shown in Table I. To bring the phosphorus content as metal down, normally more CaO and FeO would have been added to increase the phosphorus carrying capacity



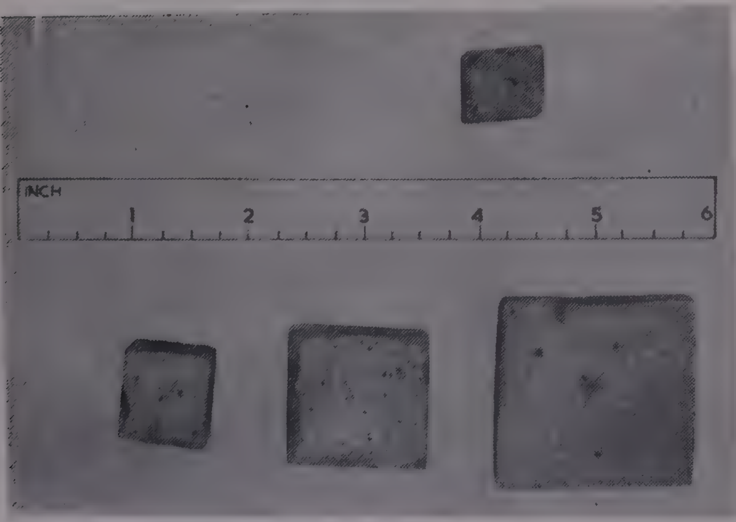
5 *Cross section of ingot of EF 77 unetched.*



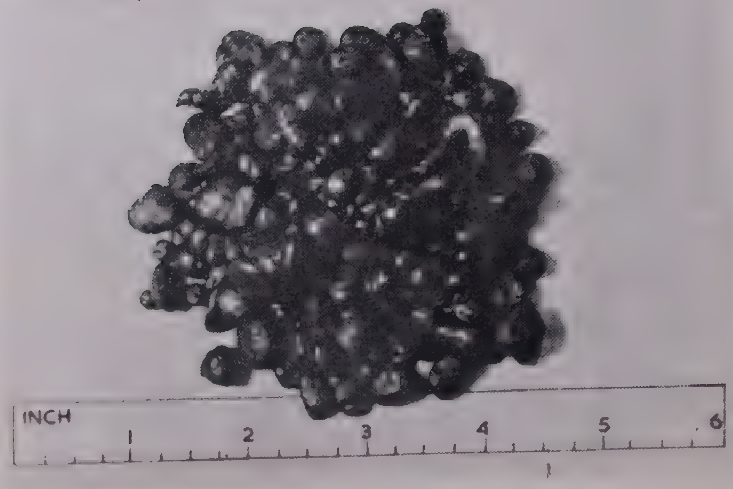
6 *Cross section of ingot of EF 78 macro-etched (50% HCl).*



7 *Cross section of ingot of EF 92 macro-etched (50% HCl).*



8 *Forged sections of EF 77 and EF 92 macro-etched (50% HCl).*



9 *Low residual iron shots.*

10 *Set up for casting iron shots.*

of the slag. But it was considered that this procedure may yield bulky slag volume which may cause localised intense heating under the electrodes in the electric arc furnace, which may lead to phosphorus reversion. The process of two oxidising slags was, therefore, adopted. The second oxidising slag made the process of subsequent dephosphorisation simple without any possibility of phosphorus reversion and phosphorus contents as low as 0·003–0·009% were obtained in the ingots of heat No. EF 83 and EF 87.

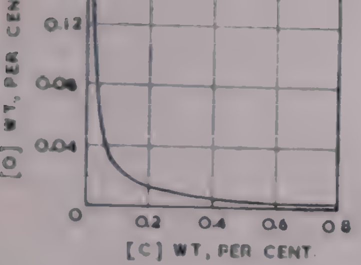
It has been observed that the phosphorus content of all the ingot sample of different heats are somewhat more than their last bath samples as shown below :

TABLE IV Phosphorus content of the last bath samples and ingot samples of different low residual and soft iron heats.

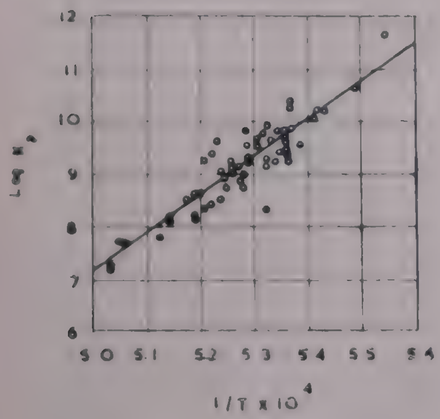
Heat No.	Last bath sample P %	Ingot sample P %
EF 77	0·0063	0·016
EF 78	0·003	0·006
EF 83	—	0·0036
EF 84	0·008	0·013
EF 87	0·0012	0·004
EF 92	0·009	0·0094
EF 94	0·003	0·007

Such rise in the P% in the cast ingots may be attributed to (i) incomplete slag off in the oxidising stage (ii) the final deoxidation of the bath which is never fully deoxidised and (iii) to some change in the slag basicity during tapping in the fire brick ladle.

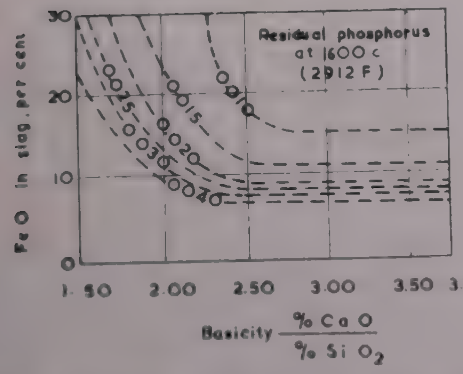
Attaining of carbon percentage of the order of 0·02% did not give any real difficulty. Oxygen lancing was done



11 *Equilibrium between carbon and oxygen at 1 600 deg. C. (Vacher and Hamilton)*[8]



12 *Effect of temperature on phosphorus equilibrium constant. (Derge and Tenenbaum)*[10]



13 *Schematic curves showing approximate effect of slag lime-silica ratio and slag FeO on residual phosphorus. (Derge and Tenenbaum)*[13]

both in the initial oxidising stage and also during the latter part in cases where some carbon pick up had been reported in the bath analysis. Log schedule of EF 77 given in Table I is an example where oxygen was lanced only in the latter stages.

Sulphur removal in steel is known to take place according to the following equations.

$$FeS + CaO = CaS + FeO \quad (3)$$
$$EeS + MnO = MnS + FeO \quad (4)$$
$$FeS + MgO = MgS + FeO \quad (5)$$

The removal of sulphur is quicker in case of equation (3) than No. (4) and (5) in view of the higher basicity of calcium oxide. In order that the reaction moves in the forward direction, it is necessary that there is very low oxide content in the bath i.e. the reaction is more favourable under highly reducing conditions, which can be maintained by the addition of normal reducing agents such as carbon, ferro-silicon, aluminium, etc. Carbon, however, in the present case cannot be used because the aim is to produce low carbon iron. Hence the choice is left between FeSi and Al. The deoxidation by FeSi is likely to produce an appreciable residual silicon in the iron which may not be suitable for using the iron as a raw material for certain special alloys. Hence attempts were made to use aluminium alone and also in conjunction with ferro-silicon for deoxidation.

Thus removal of sulphur was studied by different techniques in the reducing period namely :

(1) Ferro-silicon deoxidation, removal of the reducing slag, fresh lime slag formation, oxygen blow—6 minutes, and final aluminium deoxidation (EF 77).
(2) Ferro-silicon deoxidation, reducing slag off, fresh lime slag formation, oxygen blow (6 min.) slag off, fresh lime slag and aluminium deoxidation (EF 78).
(3) Aluminium deoxidation. (EF 83, 84 and 87)
(4) Ferro-silicon deoxidation, reducing slag off, fresh lime slag formation, oxygen blow (1 min.) and aluminium deoxidation. (EF 92)

From the final analyses result (Table II), it has been observed that sulphur levels lower than 0·02% could be obtained only in cases where ferro-silicon had been used for deoxidation—where SiO_2 is one of the slag constituents. Heats EF 83, 84 and 87 where no ferro-silicon deoxidation had been employed, no reduction of the sulphur contents of bath was observed in the second stage (reducing period). A typical case is shown in Fig. 4. Low carbon iron thus produced had silicon content of the order of 0·1% or more. To lower the silicon content, ferro-silicon deoxidised reducing slag was replaced by a fresh lime slag and the bath was blown with oxygen for desiliconisation prior to final deoxidation by aluminium. Later attempts were made to cut short the sulphur refining period by straight aluminium deoxidation after running off the oxidising slag, but in these cases, the final sulphur in the melt could not be reduced to levels lower than 0·02%. The observation that silicon accelerates the sulphur activity in the slag which results in lower sulphur content of metal, is in conformity with the results of earlier authors.[14, 15]

Fisher[15] also found that the addition of silicon to the melt produced a sharp decrease in the sulphur content of iron-sulphur melts having a carbon content in the range 0·15-4·5%. Sherman and Chipman[16] have also shown that the solubility of sulphur is much higher in iron in the absence of carbon and silicon therein. The data indicate that sulphur concentration in iron is 5 times more than in pig iron at the same temperature.

For a graphical representation of the sulphur and phosphorus removal in the melts attempts were made to illustrate the effect of different melting practice on their elimination (Figs. 1 to 4). It is interesting to note the effect of two types of reducing method :

1. Ferro-silicon deoxidation, oxygen blow and aluminium deoxidation (Figs. 1, 2 and 3).
2. Aluminium deoxidation only (Fig. 4).

In the first case, final sulphur is lowered and it is influenced by all the three treatments individually except in Fig. 3 where the effect of oxygen blow was not noticeable due to a short blowing period of 1 minute : while in the second case of aluminium deoxidation, there was no decline in the sulphur content of the bath throughout the reducing period. From Figs. 1, 2 and 3 relating to ferro-silicon deoxidised heats, it can be seen that there is a steep fall in sulphur content of the metal while in Fig. 4—aluminium deoxidised heat, the sulphur content of metal remains unaltered. Such an effect of silicon on desulphurisation is supported by the previous workers as mentioned earlier.

The ingot structures of these heats can be easily explained on the basis of their mode of smelting and teeming. The sound cross-section of heat No. 78 (Fig. 6) compared to heat No. 77 (Fig. 5) is due to the slag off operation after oxygen lancing i.e. most of the iron oxide formed during lancing process had been removed and

TABLE V Impurities in soft magnetic iron (percentage by weight)

Sample	C	S	P	Mn	Si	N	O	Total impurities
H_2 Treated (Cioffi)	0·005	0·003	0·004	0·028	0·0012	0·001	—	0·04
H_2 Treated (Cioffi, Williams and Bozorth)	0·008	0·001	—	<0·001	<0·002	—	<0·001	<0·02
Swedish	0·02	0·005	0·04	<0·01	0·02	—	—	0·1–0·3
Charcoal iron	0·06	0·01	0·07	—	0·04	—		

TABLE VI Chemical composition of imported and experimental soft iron

Sample description	C%	S%	P%	Mn%	Si%	N%	O%	Al%
Imported	0·06	0·003	0·03	0·024	0·08	0·008	0·195	—
NML product (i)	0·03	0·0095	0·0094	0·04	0·12	0·0053	0·017	0·21
(ii)	0·02	0·012	0·016	0·053	0·07	0·005	0·045	Trace

aluminium sticks were efficiently employed for deoxidation of bath. On the other hand heat No. 92 exhibited ound structure (Fig. 7) but due to a slightly modified method. In this case, after removing the reducing slag the bath was oxygen lanced for one minute only instead of 6 minutes as in case of heat No. 77. All the silicon could not thereby be removed and again aluminium sticks were effectively used for deoxidation of the melt. Incomplete removal of silicon from the bath resulted in better desulphurisation with the result that sulphur had been below 0·01% and aluminium reported was as high as 0·2 per cent.

The difference in forgeability of the three ingots can be explained on the basis of their composition mainly on the Mn/S ratio in the ingots. Absolute non-forgeability of Heat No. 78 may be due to its low manganese and sulphur ratio, less than one. Difficulty in forging of heat No. 77 might be due to the charge being slightly over-oxidising while heat No. 92 had a sound structure since the central porosity had got welded during forging. Thus, it is felt that for good forgeability of such low residual irons, silicon content may be held at about 0·1 per cent and manganese and sulphur ratio may be maintained about five (preferably between 5 and 7). Here, it may be mentioned that though heat No. 94 satisfied the Mn/S ratio yet it could not be easily forged due to a cross-ssection similar to that of heat No. 77.

Iron is used universally as a soft magnetic material in DC circuits where high permeability are required with the lowest possible magnetising field. The magnetic properties, however, depend on the chemical composition and treatment given to soft iron. Impurities such as carbon, sulphur, oxygen and nitrogen when present in small quantities exercise highly deleterious effects on its magnetic properties. To have the best possible magnetic properties from iron, it is generally desirable to eleminate these elements either during melting operation or during subsequent anneal refining treatments, such as by hydrogen treatment. The impurities observed by Cioffi, Williams and Bozorth[17, 18] in hydrogen treated iron and Swedish charcoal iron as summarised by Brailsford[19] are tabulated above :

Tables VI and VII compare the chemical composition and magnetic properties determined at the National Metallurgical Laboratory of imported soft iron samples obtained from Post and Telegraphs Workshop, Calcutta, and those of the soft iron produced at the National Metallurgical Laboratory. The magnetic tests were conducted ballistically.

In order to ascertain whether the oxygen blow in the reducing period helped in lowering the nitrogen content of the melt, nitrogen contents in the iron of different heats were analysed as given in Table II. However, there was not much difference in their nitrogen contents. Heat No. 83, 84 and 87, where no oxygen was blown in the reducing period, compare quite closely in respect of nitrogen content with melt Nos. 77, 92 and 94 where oxygen lancing had been done. It may also be noted that 1 minute and 6 minutes of oxygen blow in case of heat No. 92 and 94 respectively did not show any appreciable change in the nitrogen content. All this may be attributed to the oxidising nature of the bath till the final melting and/or tapping of the iron.

TABLE VII Magnetic Properties* of Imprted and Experimental Soft Iron.

Sample Description	Coercive force (Oersted)	Saturation Induction (Gauss)	Max. Permeability.	Remanence (Gauss)
Imported	1·15	19 509	4 000	10 350
NML Product				
(i)	1·1	18 857	—	—
(ii)	1·4	19 130	—	—

*(The experimental set up employed is not specifically designed for testing high permeability materials, the accuracy of the measurements will not be better than 10%)

It can thus be stated that for soft magnetic materials, low-carbon iron can best be manufactured by ferro-silicon deoxidation of the melt. After the usual reducing slag period, when required sulphur has been attained, the bath is ready for final deoxidation with aluminium to give the grain coarsening effect.[20]

Conclusions

1. Electric arc furnace can be used for making low residual soft iron for use as the starting raw material for the production of special steels and alloys and soft magnets.
2. The melt can be cast in the form of shots for ease of transport, handling and melting for making special steels and super alloys.
3. For shot making, the residual elements including silicon and manganese can also be reduced to further lower limits. For forging quality residual iron (suitable for soft magnets), silicon content can be raised to 0·1% which will help in eliminating the sulphur to still lower levels and thus allow the manganese content to be kept low in order to maintain the requisite Mn/S ratio.

Acknowledgement

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Thermal Beneficiation of Low Grade Chrome Ore from Enuconda Deposits, West Godavari District, Andhra Pradesh

Sipra Samanta
R. N. Misra
P. P. Bhatnagar

A low grade chrome ore from Enuconda mines of West Godavari District, Andhra Pradesh, which could not be upgraded to meet the specifications for metallurgical grade by conventional physical ore-dressing methods has been successfully beneficiated by thermal benefication methods. A table concentrate of the ore containing 40·83% Cr_2O_3, 22·19% total iron, 16·9% Al_2O_3, 3·22% SiO_2, 7·5% MgO, 1·2% CaO and initial Cr : Fe ratio of 1·23 : 1 was used for the beneficiation tests. It was possible to increase the Cr : Fe ratio of the ore to well above 10 : 1 with more than 90% chromium recovery by preferential solid state reduction of chrome ore and subsequent removal of reduced iron by acid leaching. The briquettes containing —100 mesh (B.S.S) ore and —170 mesh (B.S.S) coke were reacted at 1250°C for 2 hours and the reduced ore was leached with dilute sulphuric acid at 100°C. Controlled leaching conditions have also been found to yield a metallurgically suitable beneficiated product with almost full chromium recovery.

ONE of the essential pre-requisite for a metallurgical grade chrome ore is that it should possess a chromium : iron ratio of at least 2·8 : 1. Most of the low grade Indian chrome ores possess low Cr : Fe ratio and cannot be upgraded by physical methods of beneficiation since the oxides of iron and chromium are chemically combined in the chrome spinel. These ores can be used either for metallurgical purposes after preferential removal of iron by thermal or chemical methods or for the production of chrome based chemicals by suitable chemical methods and to some extent in chrome-magnesite refractories.

The chemical treatment for the production of chromium salts consists in either the use of alkalies, acids or by chlorination. By alkali processes, thechromium is converted into a water soluble chromate which may be used to produce chromium sesquioxide. The chromium sesquioxide so obtained can be blended witn the low grade ore to improve the Cr : Fe ratio of the latter. In the acid process, the low grade ore is leached with sulphuric acid. A basic chromium sulphate is formed by pressure leaching with controlled amonnt of acid which can be roasted to produce chromium sesquioxide. Leaching in the presence of chromic acid and subsequent electrolytic oxidation of the leach liquor produces chromic acid which can either be reduced to chromium sesquioxide for blending with low grade ore, or it can be suitably electrolysed to yield metallic chromium. Chlorination has also been reported to be useful for separation of iron and chromium.[1-4]

Thermal methods for beneficiation of low grade chrome ores consist in either alteration of the ore or preferential reduction of iron from the ore followed by subsequent separation. The ore can be altered by smelting with suitable fluxing material, and the chromium rich mineral can then be subsequetly separated by physical methods or acid leaching. Selective reduction of the ore by electric smelting has been reported[5] to produce a chromium rich slag with workable Cr : Fe ratio and a high chromium pig iron is obtained as a by-product. Thermodynamic consideration[6] indicates that chromium reduction is inevitable at high temperatures with carbon under normal working conditions. Selective reduction can be carried out in solid state at a comparatively lower temperature without reducing chromium oxide. The metallic iron can be removed by acid leaching leaving behind a chromium rich residue with high Cr : Fe ratio.

Systematic research work has been undertaken at the National Metallurgical Laboratory utilising gaseous[7] as well as solid carbonaceous reducing agents for selective solid state reduction of chromite. The reduced iron is subsequently removed by leaching with dilute sulphuric acid. It has been observed by Misra and Bhatnagar[6] that solid reducing agents are more selective for the reduction of iron. This paper records the reserch results of thermal beneficiation by solid state reduction of a low grade chrome ore from Enuconda deposits of West Godavari district, Andhra Pradesh.

The ore sample

A sample of chrome ore from the Enuconda deposits, West Godavari district, Andhra Pradesh, was taken up for beneficiation studies. The reserves of float ore are estimated at about 10,000 tons and a few lakh tons below the surface.[8] The analysis of the ore as received is given in the following page.

Miss Sipra Samanta, Messrs R. N. Misra and P. P. Bhatnagar, National Metallurgical Laboratory.

Cr_2O_3	38·0
FeO	26·2
Soluble Fe	1·36
SiO_2	8·3
Al_2O_3	15·4
MgO	10·3
CaO	1·9

Petrological examination[8] of the chrome ore sample showed that chromite was the chief mineral followed by orthopyroxenes (hypersthene and enstatite,) plagioclase feldspar, biotite with small amounts of antigorite, ilmenite and traces of goethite and haematite. Chromite grains were fairly coarse (0·243 mm) whilst average grain size of gangue is of the order of 0·162 mm. The relative proportions of chromite and gangue in the composite sample worked out to be 60 to 65% chromite and 35 to 40% gangue. A fair liberation of the chromite can be achieved if the ore is crushed to about-65 mesh size.

Physical methods of beneficiation investigated by Narayanan et al[8] have included tabling, floatation and magnetic separation. Tabling at —72 mesh (B.S.S.) produced a concentrate containing 43·85% Cr_2O_3 and 29·25% FeO with a Cr : Fe ratio of 1·3 : 1, and 82·9% chromite recovery. Floatation or magnetic separation methods could not improve the grade of the ore. As is obvious from the petrological examination, a chemical attack on the chrome spinel is necessary to bring about a change in the Cr : Fe ratio of the ore.

A table concentrate of the ore was used for this investigation. The concentrate was obtained at —72 mesh (B.S.S.) with an average grain size of 0·1207 mm having an analyis as follows :

	%
Cr_2O_3	40·83
Fe total	22·19
Al_2O_3	16·9
SiO_2	3·32
MgO	7·5
CaO	1·2
Cr/Fe ratio	1·23

Procedure

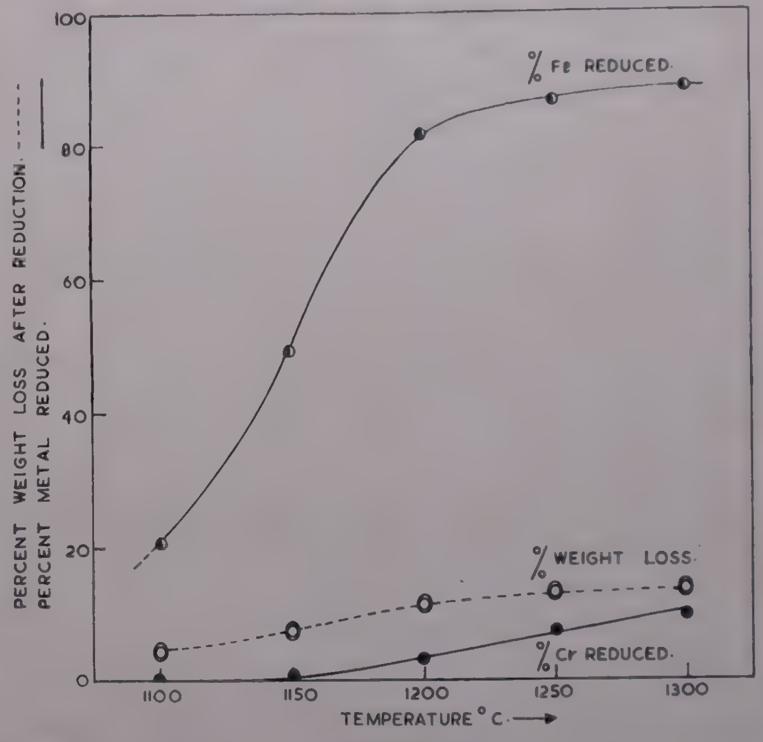
Weighed amounts of chrome ore concentrate and powdered coke were briquetted with 1% dextrine in presence of 2% moisture under a pressure of 5 000 psi. The coke sample used in this investigation contained 75·5% fixed carbon, 22·53% ash and 1·95% volatiles. The amount of coke for preparing the mix was calculated on the basis of iron oxide present in the ore. In this case, the ore : coke ratio was fixed at 1 : 0·074. The briquettes were air dried at 110°C. The dry briquettes were placed inside a tightly covered crucible and heated at a desired temperature for a specific period. The reduced briquettes were cooled to room temperature under cover and crushed to —100 mesh (B.S.S) size for acid leaching. Leaching was continued for one hour with 10 gm of reduced ore and 100 ml of 10% (by volume) sulphuric acid under boiling condition. The slurry was filtered and the residue was thoroughly washed till it was freed of the acid. The leach liquor was analysed for iron and chromium. The residue was air dried at 110 C and weighed. Chromium recovery and Cr : Fe ratio of the beneficiated product were calculated from leach liquor analysis or direct analysis of the residue.

Results

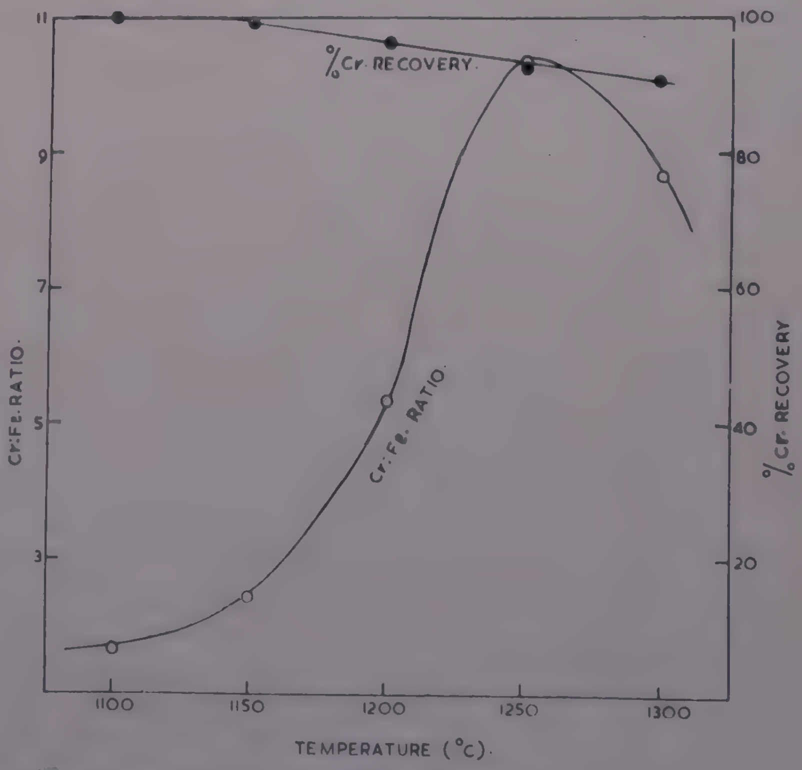
Effect of temperature on reduction

Briquettes with —72 mesh (B.S.S) chrome ore and at different temperatures varying from 1100°—1300°C. The Cr : Fe ratio, percentage of chromium recovery of the residue and the percentage of dissolved chromium and iron on leaching are graphically shown in Figs. 1 and 2.

It would be observed that the percentage of iron dissolved increased rapidly from 20·29 at 1100°C to 86·92 at 1250°C, whilst there was no appreciable removal of chromium on leaching the product reduced up to 1150°C. With the increase of the temperature of reduction to 1300°C, the chromium recovery gradually decreased from 99·45% at 1150°C to 90·83% at 1300°C. Consequently, the Cr : Fe ratio of the ore rapidly rose from 1·69 at 1100°C to 10·39 at 1250°C. Beyond 1250°C, however, there was no further appreciable rise in iron while the reduction of chromium proceeded steadily thereby recording a fall in the Cr : Fe ratio in the beneficiated products.



1 *Effect of temperature on the extent of reduction.*



2 *Effect of temperature on Enuconda chrome ore.*

It was observed that the optimum temperature of reuduction was 1250°C, whereby a product with a Cr : Fe ratio of 10·39 and chromium recovery 92·98% was obtained.

Effect of particle size of the ore concentrate

Effect of particle size of the chrome ore on the beneficiation was studied using briquettes containing chrome ore concentrate of different particle sizes ranging from —72 to —200 mesh (B.S.S.). These briquettes were reacted at 1250°C for 3 hours. The size of coke was kept constant at —200 mesh (B.S.S.). The Cr : Fe ratio and the chromium recovery are recorded in Table I. The average particle diameter recorded in Table I were determined by the method of sieve analysis.

TABLE I Effect of particle size of the ore on reduction.
Temperature 1 250°C
Period of reduction 3 hours
Ore : Coke ratio 1·074

Sl. No.	Size of ore (B.S.S.)	Average particle diameter (mm)	Cr : Fe	% Chromium recovery
1	— 72 mesh	0·0978	6·38	93·85
2	—100 ,,	0·0734	10·32	94·93
3	—120 ,,	0·0686	10·16	94·61
4	—170 ,,	0·0488	9·10	93·91
5	—200 ,,	0·038	7·87	94·14

Table I indicates that the Cr : Fe ratio of the ore increases from 6·38 to 10·32 with decrease in average particle diameter of chromite from 0·0978 mm to 0·0734 mm and remains almost unchanged till the particle size is further reduced to 0·0488 mm. Thereafter, the Cr : Fe ratio records a fall to 7·87, with an average particle diameter of 0·038 mm. The chromium recovery was not very much affected by variation in particle size and was restricted to about 94% on the average.

Effect of particle size of coke

A set of experiments were carried out with briquettes containing —72 mesh (B.S.S) size of the ore concentrate and different sizes of coke in the range of —72 to —200 mesh (B-S.S). All other conditions for reduction were kept similar to the previous set of experiments. The results of these experiments are presented in Table II.

TABLE II Effect of size of coke on reduction.
Temperature 1 250°C
Period of reduction 3 hours
Average particle diameter of ore 0·0734 mm

Sl. No.	Size of coke (B.S.S.)	Average particle diameter (mm)	Cr : Fe ratio	% Chromium recovery
1	— 72 mesh	0·1084	6·24	96·01
2	– 100 ,,	0·0786	6·08	95·81
3	—120 ,,	0·0746	6·62	96·01
4	—170 ,,	0·0566	6·89	95·57
5	—200 ,,	0·038	6·60	96·61

Table II shows that the chromium recovery remains steady at about 96% with variation of coke size in the —72 to —200 mesh (B.S.S.) range. The Cr : Fe ratio increased from about 6 to a slightly elevated value of 6·6 with decrease in the particle size from —72 to about —120 mesh (B.S.S.) and smaller sizes.

Experiments were carried out at 1250°C using —100 mesh (B.S.S.) size ore concentrate (average particle diameter : 0·0734 mm) and —170 mesh (B.S.S.) coke powder (average particle diameter : 0·0566 mm) as the charge. Reactions were continued for different periods ranging from 30 to 180 minutes. Results of these experiments are graphically represented in Fig. 3.

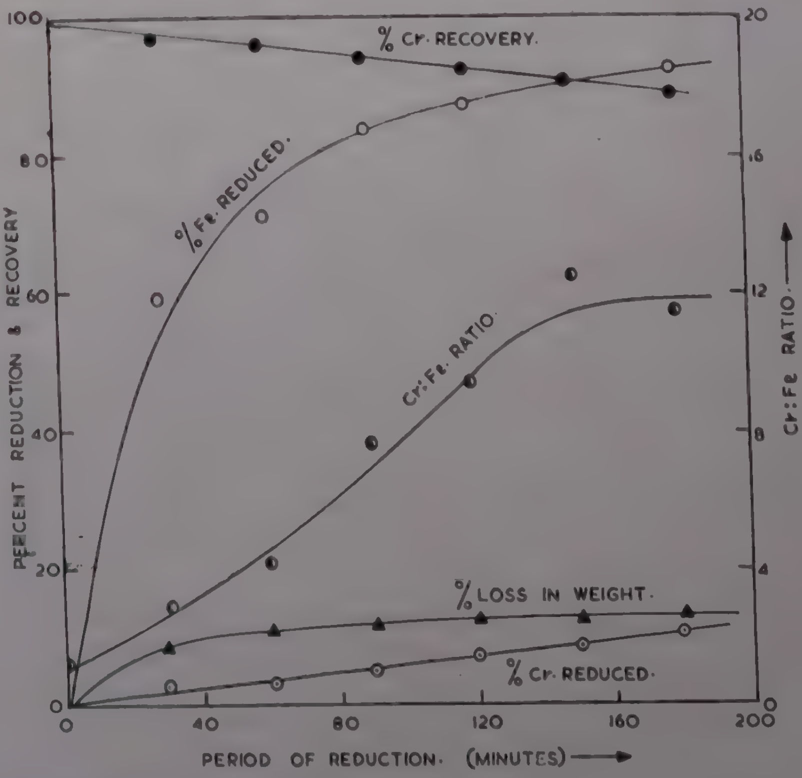
It would be observed that iron is reduced upto the extent of 59% during the initial thirty minutes of the experiments and increases gradually to 92% as the reaction is prolonged upto three hours. Reduction of chromium steadily increases from 3·5% to 10·2% as the period of reoction is increased from 30 to 180 minutes. The Cr : Fe ratio of the ore is improved to 2·96 within the initial thirty minutes and continues to increase steadily upto about 12 with increase in period of reduction to 150 minutes and thereafter remains almost steady. Chromium recovery recorded a fall from 96·5% to 82·79% as the reaction period is prolonged from 30 to 180 minutes.

Leaching characteristics

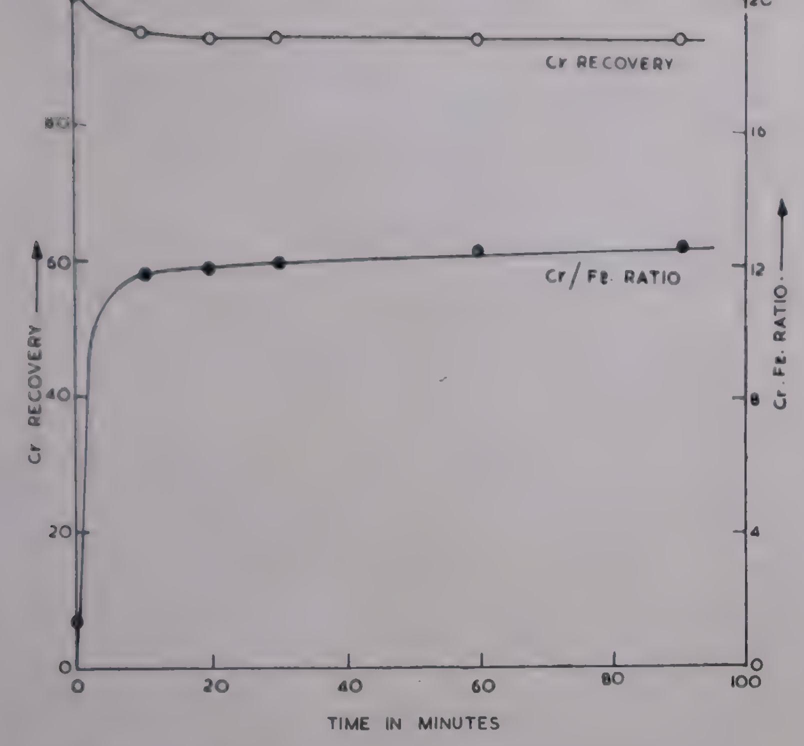
A sample of reduced chrome ore concentrate was obtained by reducing—100 mesh (B.S.S.) ore concentrate with—170 mesh (B.S.S.) coke at 1250°C for 2½ hours. The reduced product was crushed to—100 mesh (B.S.S.) size for leaching studies. A stock solution of 10% (by volume) sulphuric acid was prepared and standardised titrimetrically. The strength of this acid corresponded to 176·6 gm H_2SO_4/litre.

Progress of leaching under boiling conditions was studied by leaching weighed amounts of reduced ore with the stock acid solution for different periods. The reaction was arrested by quick cooling and diluted with large volume of water. The slurry was quickly filtered under suction. The results of these experiments are shown in Fig. 4, which indicates that practically the leaching is over well within 30 minutes duration under boiling conditions.

Leaching experiments under boiling conditions were carried out with varied reduced ore to acid ratio to find



3 *Kinetics of reduction at 1250°C.*



4 *Study of kinetics of leaching of Enuconda chrome ore.*

out any effect on the suppression of chromium dissolution. The pulp density was, however, kept unaltered by dilution. It has been concluded by two of the authors in an earlier publication[7] that the efficiency is independent of extent of dilution of acid, and hence is not expected to have an adverse effect in the present procedure. The results are tabulated in Table III.

TABLE III Effects of amount of acid on leaching

Sl. No.	*Acid ratio	%Soluble metal Fe	%Soluble metal Cr	Cr : Fe ratio	%Chromium recovery
1	10 : 9	18·9	0·525	6· 0	98·24
2	1 : 1	19·45	1·475	6· 6	95·04
3	9 : 10	19·87	1·825	7·14	93· 9
4	1 : 10	21·36	1·875	12· 3	93·67

$$\text{*Acid ratio} = \frac{\text{Theoretical amount of acid required}}{\text{Actual amount acid added}}$$

Table III indicates that 98% chromium recovery with a Cr : Fe ratio of 6·0 is attainable by using 10% less than theoretically required amount of acid. On leaching with equivalent amount of acid the chromium recovery falls to 95% and continues to fall upto 93·7% when a ten fold excess acid was used for leaching.

Discussion

Studies on the effect of temperature on reduction of the chrome ore indicated that iron reduction is markedly dependent on temperature below 1250°C and assumes more or less a steady value thereafter. Reduction of chromium is not effected below a temperature of 1150°C and is perceptible only above 1200°C. The chromium reduction steadily increases in a linear fashion with increase in temperature and the relationship can be expressed as,

$$A = 0{\cdot}0648\ T - 75{\cdot}06 \qquad \ldots (1)$$

where A and T represent the percentage of chromium reduction and temperature in degrees centigrade respectively.

The increased chromium reduction with increasing temperatures leads to a simultaneous decrease in the chromium recovery. The relationship between chromium recovery and temperature is found to satisfy a linear equation of the type,

$$B = 168{\cdot}45 - 0{\cdot}06\ T \qquad \ldots (2)$$

where B and T represent the percentage of chromium recovery and temperature in degree centigrade. The relationships in (1) and (2) are valid only within the temperature range of 1150° – 1300°C.

The Cr : Fe ratio of the ore is dependent on the extent of reduction of iron and chromium and increases with rise in temperature so long as the rate of reduction of iron with temperature remains higher than the rate of chromium reduction with temperature. Slopes of the respective curves in Fig. 1 indicate that beyond 1250°C the reduction of iron remains virtually unchanged while chromium reduction goes on steadily increasing. As a consequence, the Cr : Fe ratio of the ore starts deteriorating above 1250°C. The optimum temperature of reduction can, therefore, be fixed at 1250°C.

Investigations on the effect of particle size of the reactants reveal that the ore should be crushed to –100 mesh (B.S.S.) and coke to any size below –120 mesh (B.S.S.) for reduction purpose. The chromium recovery is not very much affected by a variation in particle size of the concentrate and is restricted to about 94% on the average. It is the degree of reduction of iron oxide content of the ore which is responsible for the variation in Cr : Fe ratio with size of ore. A larger particle size is unsuitable in view of the poorer mineral liberation and is fully justified from the microscopical observations.[8] A finer size, on the other hand, can make a very compact briquette retarding the release of volatile product and thereby can hinder the reaction to proceed to completion with ease. Table I indicates that the correct size of the concentrate for reduction can be fixed at –100 to 120 mesh (B.S.S.) restricting its average particle diameter to about 70 microns.

The beneficiation process is not very much affected by alteration in coke size within the range recorded in Table II. The chromium recovery remains steady around 96%, and the Cr : Fe ratio is only slightly improved by keeping the coke size below 0·075 mm. Optimum coke size for benefication can be fixed at –120 mesh (B.S.S.) while finer size would not affect the efficiency of reduction.

The kinetics of reduction at 1250°C has been represented in Fig. 3. It is clear from the figure that during the initial stages, reduction of iron is quite rapid. Up to 60% of the total iron content gets reduced within only half an hour, while a period of two and half hours is necessary for 90% iron reduction. Chroimum reduction appears to be a linear function of the period of reduction and imparts a correspondingly inverse effect on the chromium recovery. The rate of reduction of chromium with increasing period at 1 250°C is found to follow a simple linear relationship.

$$R_{Cr} = 0{\cdot}498\ t \qquad \ldots (3)$$

where 'R_{Cr}' represents extent of reduction of chromium during a period of 't' minutes. The chromium recovery, likewise bears a similar relationship with period of reduction and satisfies the equation,

$$2{\cdot}008\ r_{Cr} = 200{\cdot}803 - t \qquad \ldots (4)$$

where r_{Cr} is the percentage of chromium recovery for a reduction period of 't' minutes. Equations 3 and 4 are valid at 1250°C, and are strictly limited to the duration within which benefication is desirable. The Cr : Fe ratio of the ore is dependent on the relative rates of reduction of oxides of iron and chromium. Since during the initial stages, the rate of reduction of iron is several times faster than that of chromium, there has been an initial rise of the Cr : Fe ratio. The Cr : Fe ratio assumes a steady value after 150 minutes due to the constancy in the value of iron reduction. In view ofthe fact that most of the iron is reduced within 150 minutes of reaction recording a steady value of Cr : Fe ratio thereafter, the reduction may be continued up to 150 minutes for maximum economical benefication of the ore.

Studies on kinetics of leaching the reduced product indicate that leaching is completed within half an hour at boiling temperature. A possible suppression of chromium dissolution by controlled acid addition is indicated from Table III. The ratio of theoretical to actual amount of acid need for suppressing chromium dissolution has been found to be of the order of 10 : 9. A complete chromium recovery can be obtained with a premium on the Cr : Fe ratio of the beneficiated ore, but this would offer ease in obtaining ferrous sulphate as by-product without any interference with chromium.

Conclusions

A low grade chrome ore from Enuconda deposit of West Godavari district, Andhra Pradesh, containing initially 38·0% Cr_2O_3, 26·2% FeO, 1·36% soluble iron, 8·3% SiO_2, 15·4% Al_2O_3, 10·3% MgO and 1·9% CaO could not be upgraded for metallurgical use by conventional ore dressing method. A table concentrate of the ore containing 40·83% Cr_2O_3. 22·19% total iron, 16·9% Al_2O_3, 3·32% SiO_2, 7·5% MgO, 1·2% CaO and a Cr : Fe ratio of 1·23 : 1 was used for thermal beneficiation tests comprising of preferential reduction of iron and its

It has been established that the chrome ore concentrate can be reduced at 1250°C for a period of two hours in briquetted form utilising—100 mesh (B.S.S.) size of ore and—170 mesh (B.S.S.) size of coke. The reduced ore crushed at –100 mesh (B.S.S.) size can be leached with 10% (by volume) sulphuric acid at about 100°C within half an hour.

Dissolution of any reduced chromium can be successfully suppressed by restricting the amount of acid to 10% less than the theoretical requirement calculated on the basis of soluble iron content of the reduced ore.

The table concentrate of the chrome ore could be upgraded to a Cr : Fe ratio of well above 10 : 1 with more than 90% chromium recovery. It is possible to achieve almost full chromium recovery with a suitable Cr : Fe ratio by proper control of leaching.

Acknowledgement

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A Comparative Study of Insulation Refractories with Special Reference to Thermal Conductivity

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Thermal conductivity and other physical properties of insulation refractories collected from various indigenous sources together with an imported sample, for comparison, have been studied with a view to help in the formulation of standard specification for insulation refractories at the request of Indian Standards Institution. The thermal conductivity apparatus was fabricated at the National Matallurgical Laboratory based on A.S.T.M. design. Due to the large number of variables involved, though it has not been possible to draw any specific conclusions, it appears probable that in the case of backing insulation, the thermal conductivity increases with alumina content whereas with type II insulation brick, the reverse trend is noticed. From this study of indigenous samples, it appears that there are few samples which could be classified as superior to type II IS 2042–1963. But unlike American and other classification of insulation refractories, we have no other suitable classification in which these bricks can fit in. Amongst the samples studied so far, there is only one silica based sample which conforms to type III of IS 2042–1963.

THERMAL conductivity of refractories has a direct influence over efficiency of the furnace. Insulation bricks should have low conductivity, whereas bricks used for inner walls of muffle furnaces, crucibles, saggars etc., should have high thermal conductivity. Similarly checker bricks, recuperators and regenerators should absorb and store the maximum amount of heat from the hot gases and then give it up to the cold gases in the reverse process. An exact knowledge of thermal conductivity behaviour of refractory materials is quite essential to the manufacturer, consuner and designer.

It is well known that other than the inherent thermal conductivity of the main raw material from which insulation refractories are made, their porosity, initial firing temperature and other process variables also affect the thermal conductivity of the fired bricks. With a view to collect data on indigenous insulation refractories 12 different samples of insulation bricks from different indigenous sources were collected through the Indian Standards Institution. For comparison a standard quality imporied hot face insulation brick was also included and their thermal conductivity, as well as other physical properties were studied. The data so collected would be useful in formulating standard specifications for insulation refractories.

Theory

Conduction, convection and radiation are the three different means by which heat tarnsfer takes place through a body or from one body to another. Refractories are made up of solid material with closed pores and open pores. Some are globular, others are tube like and yet others open all the way to the surface therefore transfer of heat is not strictly due to conduction alone. But as the pores are small, at low temperatures, heat transfer will be mostly by conduction. At high temperatures, radiation has a marked effect. Thermal conductivity is calculated from the equation

$$K = \frac{Q \times L}{A\ (t_2 - t_1) \times T}$$

where Q denotes the total quantity of heat passing through the section; A, area of cross section; t_2-t_1, difference of temperature between hot and the cold faces; T, time interval; and L, the thickness of the section. The absolute value in C.G.S. units is expressed in terms of calories/sec/sq. cm./°C diff. in tem./cm. thickness while the British Unit is B.Th.U/hr./sq. ft/°F/inch thickness.

According to Austin[1] the following factors influence the thermal conductivity of non-metallic materials.

A. *Chemical Composition :*
  1. Influence of molecular structure in pure compounds.
  2. Influence of impurity in solid solution.

B. *Physical Texture :*
  1. Porosity.
     (*a*) Total void space.
     (*b*) Size and shape of pores.
     (*c*) Size and shape of grains.
  2. Presence of a vitreous or liquid phase.
     (*a*) Total amount of the phase.
     (*b*) Distribution of the phase.
  3. Development of ceramic bond and sintering.
     (*a*) Influence of time of firing.
     (*b*) Influence of temperature of firing.
  4. Anisotropy and directional effects.

C. *Temperature.*

D. *Pressure, Stress or Strain.*

E. *Heat flow.*

The co-efficienet of thermal conductivity is by definition not independent of chemical composition, physical texture, temperature, pressure or heat flow; and according

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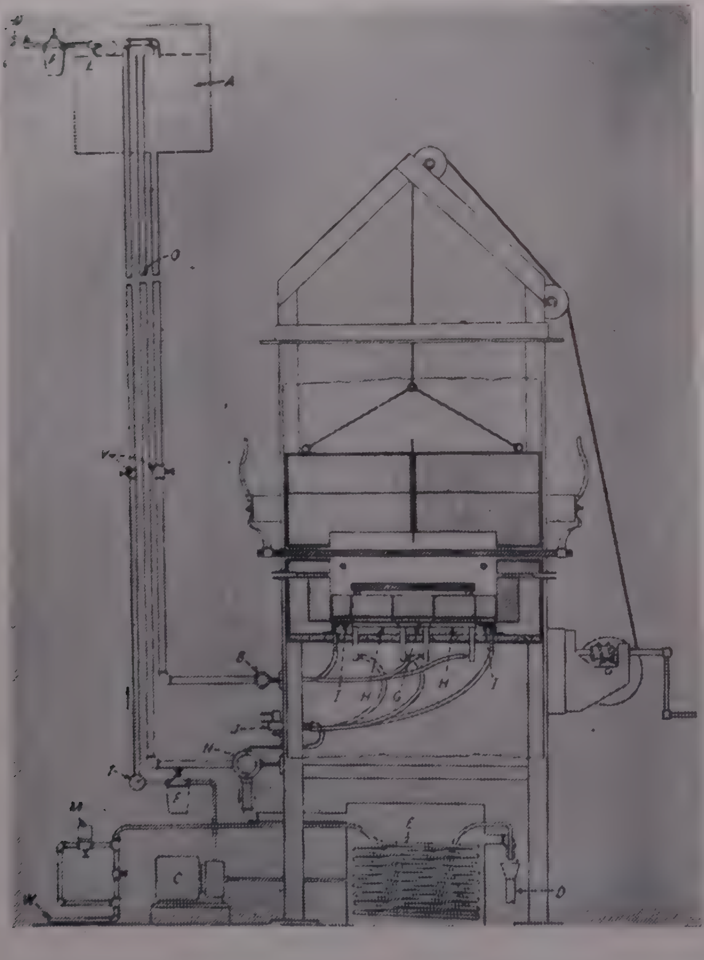
to Austin its greatest variation occurs with physical texture. In the continuous solid type in which the pores are embedded in the solid matrix, the thermal conductivity decreases linearly as the porosity increases; and in the continuous air-type in which the solid is composed of large grains and the pores are the spaces between grains, the decrease in conductivity with increasing porosity is given approximately by a rectangular hyperbola. Pore size is significant only when the pores are so large that heat transfer by radiation approaches heat transfer by conduction. The shape and the size of pores and the shape of the grains have little influence on the conductivity of an aggregate.

Firing temperature of the brick, as well as fluxing and sintering actions that generally lead to a reduction in porosity have a tendency to increase the thermal conductivity whereas an increase in porosity resulting from the combustion or volatilization of some ingredients results in a decrease in the conductivity.

In the case of single crystals and of many highly conducting refractory bodies, conductivity decreases with increasing temperatures, and is generally proportional to the reciprocal of the absolute temperatures. In the case of an amorphous body, such as glass, and of many poorly conducting refractory materials, the conductivity increases with increasing temperature and is very nearly linear.



A	*Constant head water supply*
B	*Inlet manifold and thermometer*
C	*Circulating pump*
D	*To drain*
E	*Cooling coil*
F	*Water filter*
G	*Center calorimeter*
H	*Inner guard calorimeters*
I	*Outer guard calorimeter*
J	*Micro regulating valves*
L	*Water level valve*
M	*Magnetic control valve*
N	*Outlet manifold*
O	*Overflow pipe*
T	*Thermostat (Controls M)*
V	*Valves*
W	*Water inlet*

1 *Diagram showing essential parts of thermal conductivity.*

2 *Thermal conductivity apparatus with the control panel.*

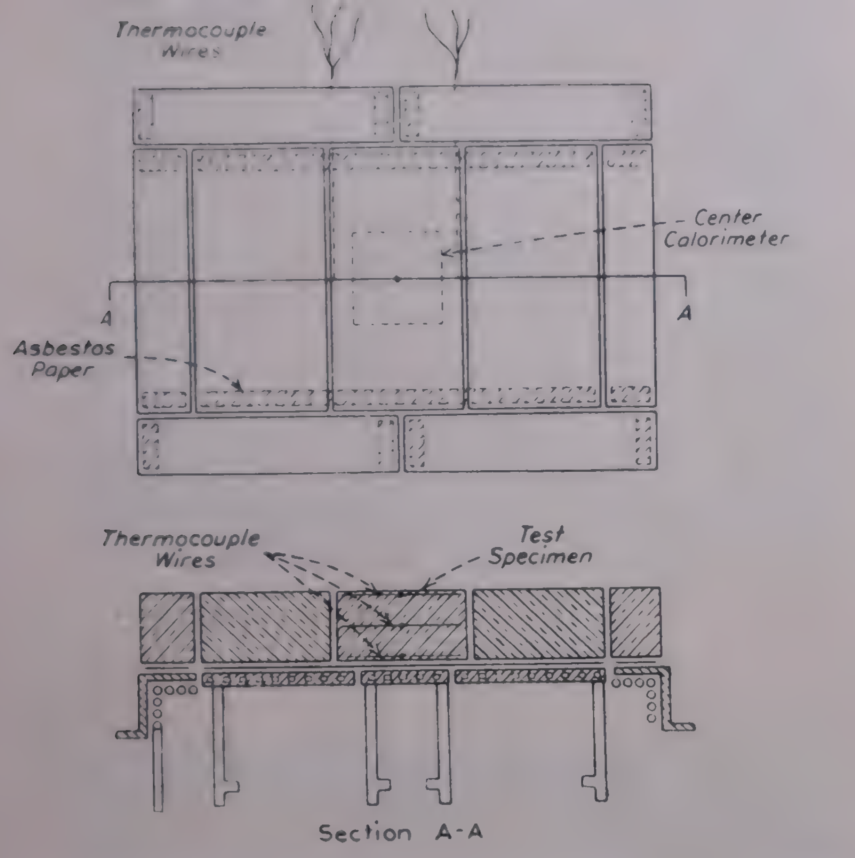
The purity of a material, the amount of impurities, and state of their incidence such as in a solid solution or as a separate phase etc. affects the thermal conductivity. Simple molecular or lattice structures are said to have a higher conductivity and most of the commercial refractories are said to show the conduction characteristics of an amorphous body, i.e. rising with temperature.

Apparatus used for measurement of thermal conductivity

The thermal conductivity values of the insulating bricks have been determined in the apparatus fabricated at the National Metallurgical Laboratory, based on the A.S.T.M. design[2]. A diagramatic view of the apparatus is shown in Fig. 1 and Fig. 2 shows the actual photograph of the apparatus with the control panel.

The furnace is heated by six air cooled globar heating elements which have a range from 400 to 2800°F. A silicon carbide slab, kept over the sample and guard bricks serves to distribute the heat uniformly and levels out thermal fluctuations. The water system for the calorimeter operates as a closed reciprocating system. Water flows down from the upper head tank through the calorimeter system and into the down tank from where it is pumped back to the head tank. A thermostat controls the temperature of water and it is set to operate at room temperature so that there is no appreciable heat transfer between the calorimeter systems and the surroundings.

The calorimeter system, with all its elaborate guard rings, is constructed in such a way that the adjacent hot and cold channels maintain uniform temperature distribution over the entire space. The central calorimeter, over which the test brick is kept, is a square of 3″ length. The flow of water in the central calorimeter and the two guard calorimeters is strictly proportional to their areas,



3 *Arrangement of the test brick, guard bricks and the thermocouples.*

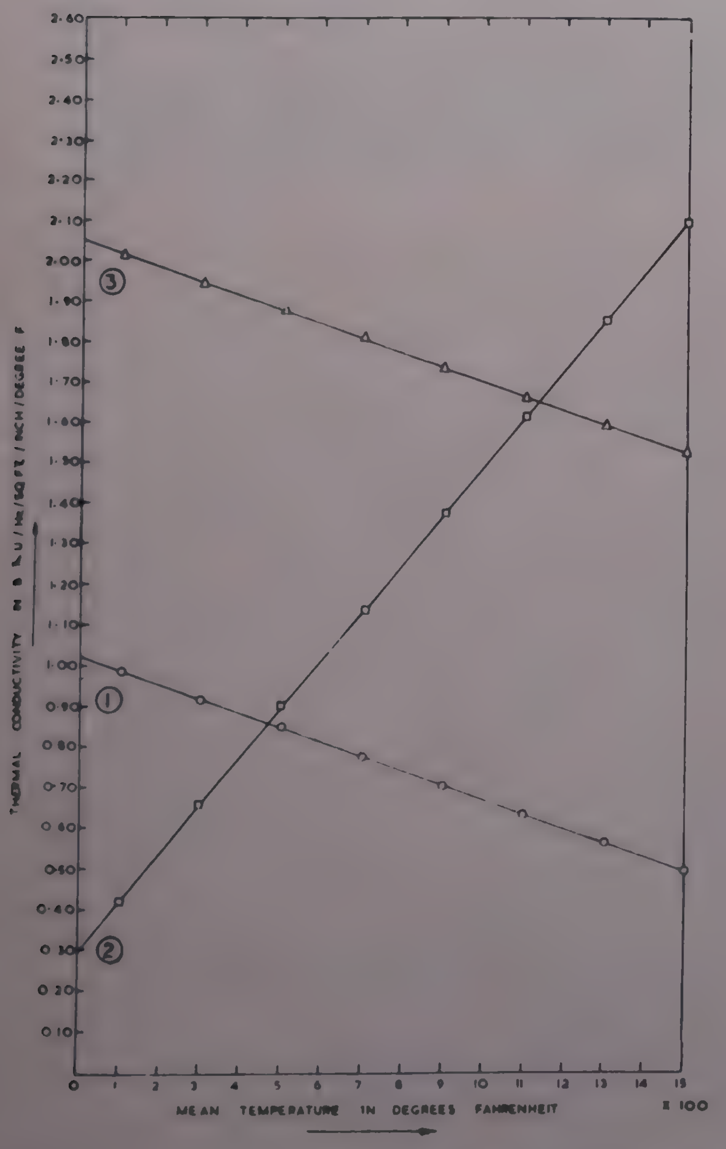
so that there may not be any thermal imbalance between the central calorimeter and the guard calorimeters.

Multiple differential thermocouples are used for measuring temperatures at different points in the apparatus. The thermocouples are threaded into the holes drilled close to the hot and cold faces, and one to the centre of the test piece for insulating bricks. For dense bricks, the couples are cemented to grooves cut along the surface of the brick.

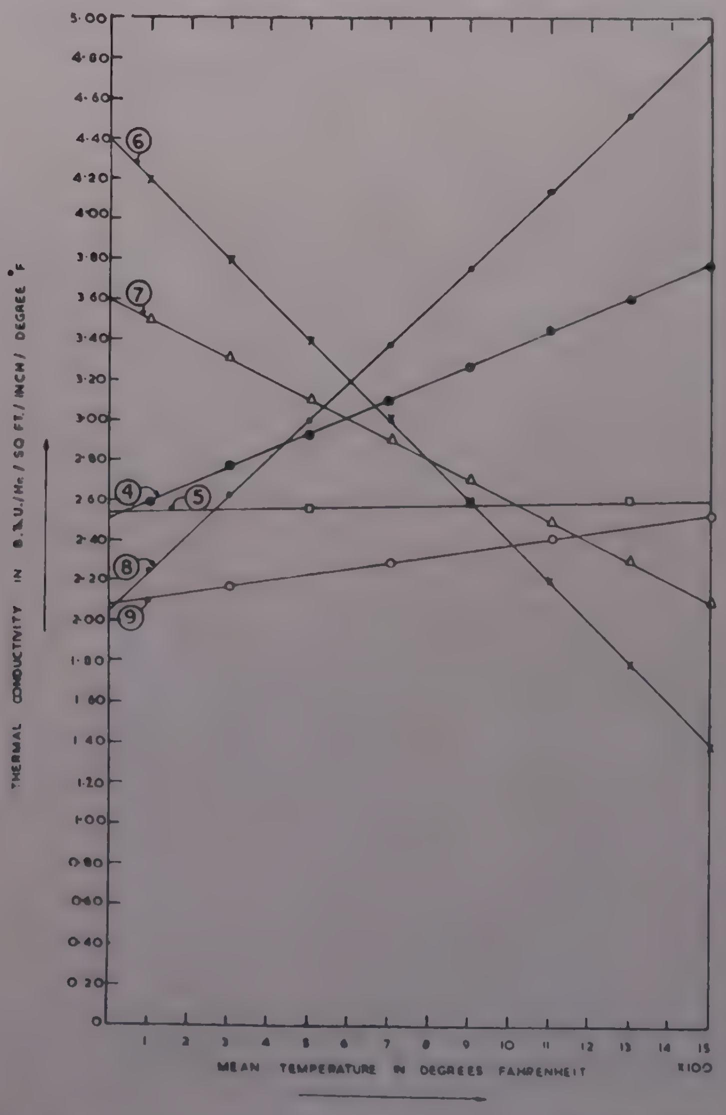
The sample consists of three 9″ straight bricks representative of the material to be tested. The central 3″ × 3″ portion of the middle brick is the test piece and the other two bricks are used as guards, one on either side, to prevent lateral flow of heat. The arrangement of the test brick, guard brick and the thermocouples have been shown in Fig. 3.

From temperature measurements at different points the dimensions of the test piece and the total flow of water through the central calorimeter, the coefficient of thermal conductivity (K) of the brick was calculated.

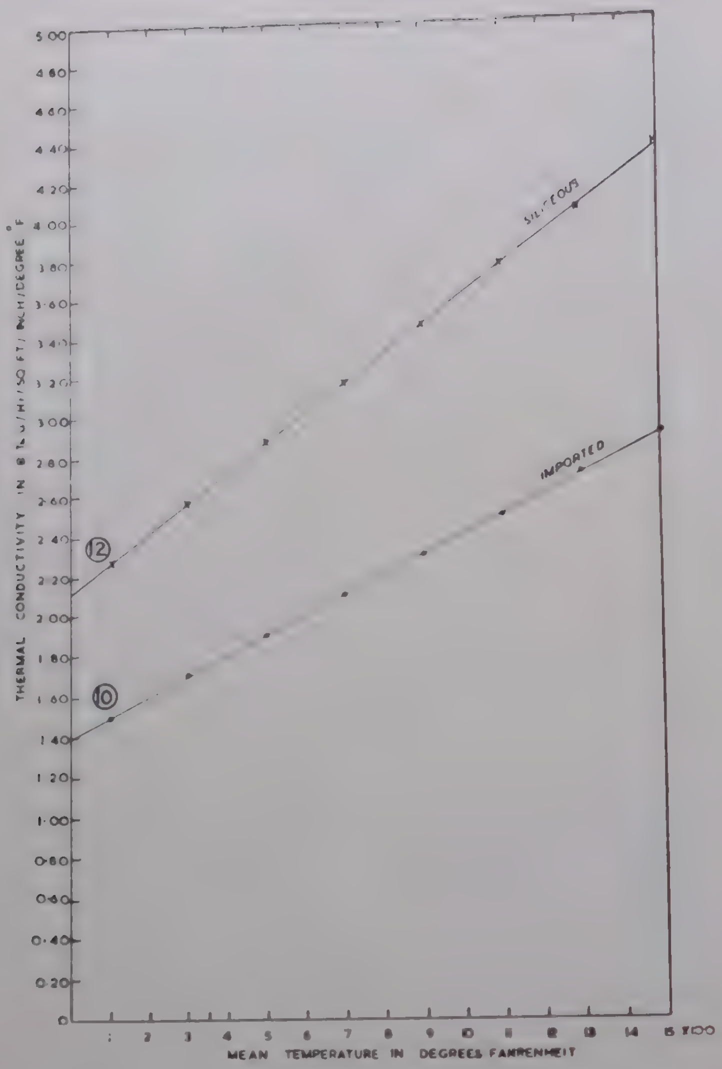
The thermal conductivity of the samples collected from different sources was determined as described above and other physical properties such as porosity, cold crushing strength, P.C.E. permanent linear change or reheat were tested according to relevant I.S. specifications (I.S. 1528–1962 and 2042—1963). Refractoriness underload was done as per IS 1528—1962 but with 10 lb/sq. inch load instead of 28 lb as these were insulating bricks. Permeability was tested as per British Standard specification No. 1902 of 1952. Chemical analysis was done as per IS 1527–1960.



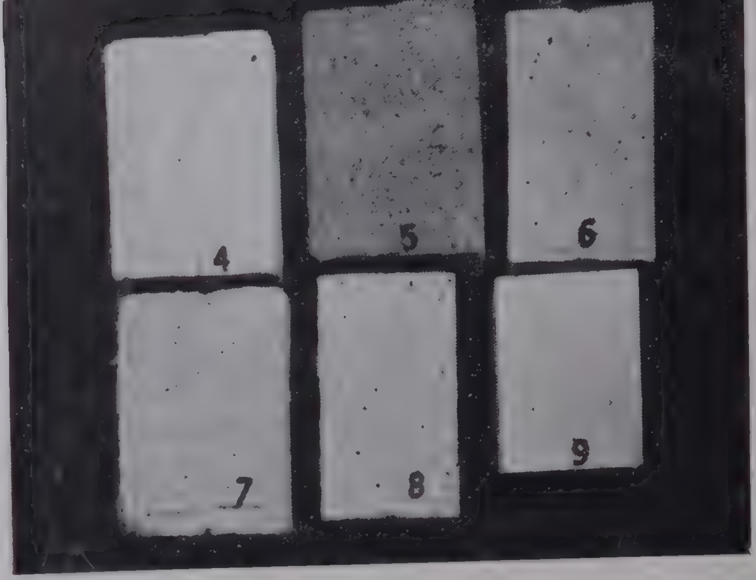
4 *Variation of thermal conductivity with temperature. Backing insulation bricks. Type 1 of I.S. 2042–1963.*



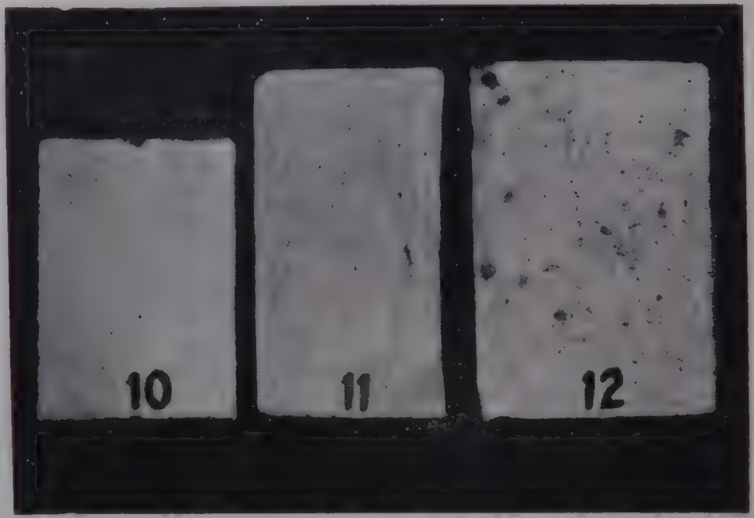
5 *Variation of thermal conductivity with temperature. Insulation bricks of type 2 of I.S. 2042–1963.*



6 *Variation of thermal conductivity with temperature (iii) silica and imported alumino-silicate hot face insulation bricks type 3 of I.S. 2042-1963.*



8 *Physical texture of low temperature hot-face insulation refractories (type 2 I.S. 2042–1963).*



9 *Physical texture of hot-face insulation refractories (type 3 I.S. 2042–1963).*

Results and discussion

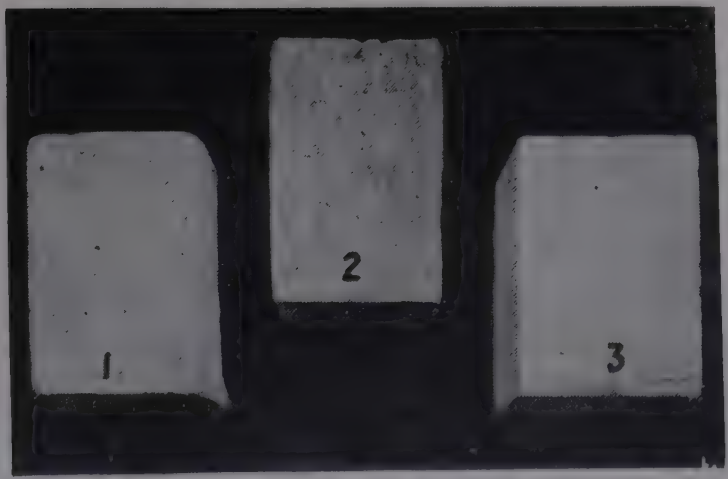
Chemical analyses and physical properties are given in Table I. Thermal conductivity values at different mean temperatures for the different samples studied are shown in Figs. 4, 5 and 6. Based on the chemical composition and quality of the samples studied, these have been classified under different headings. The texture of the bricks studied are shown in Figs. 7 to 9, where these are grouped according to their respective class.

(i) Backing insulation : Of the three samples tested in this group at the National Metallurgical Laboratory, one is of the Alumino-silicate type, and the other two have Magnesium-silicate as base materials, one being exfoliated vermiculite and the other waste mica ; the latter two have the same refractoriness and practically the same permeability.

It is well known that when the base material is the same, thermal conductivity is generally directly proportional to bulk density as well as permeability and inversely proportional to the porosity. Comparing sample nos. 1 and 2, it may be observed that permeability value of the samples are the same while the thermal conductivity values are inversely proportional to their respective porosity values. It is also observed that the thermal conductivity values are directly proportional to their respective bulk density values, though the ratio of the two thermal conductivities are different from the ratio of the two bulk densities. This difference may be due to the difference in the conductivity of the solid material, as one is exfoliated vermiculite and the other is exfoliated waste mica. From texture shown in Fig. 7, it may be seen that sample no. 1 has more uniform and rounded grains whereas sample no. 2, being a mica brick, has flaky particles bonded with fire clay.

As regards cold crushing strength, it is observed that sample no. 1 which is an unfired brick, with vermiculite base, has better strength than the mica based brick.

Sample No. 3 which is of alumino—silicate base has a much higher thermal conductivity and comparatively



7 *Physical texture of backing insulation refractories.*

lower crushing strength, which may be attributed to the manufacturing method adopted in obtaining high porosity at the expense of crushing strength. The permeability is also higher in comparison to other two samples. This also may be partially responsible for the higher thermal conductivity value. Being of fireclay base, the conductivity of the solid material is perhaps much higher than the conductivity of exfoliated vermiculite or exfoliated mica and its refractoriness is also higher than the other two. But all the same, reheat test carried out at 1250 C indicates that this brick cannot be used as a hot-face insulation at 1250 C. At the most, as indicated by the refractoriness underload value, it could perhaps be used upto 1000 C whereas in the case of samples nos. 1 and 2 they are definitely meant as backing insulation. Sample no. 3 has an open texture and the grains do not appear to be bonded to each other well, resulting in low crushing strength.

TABLE I The physical and chemical properties of insulation refractories

Sl. no	App. porosity %	B.D. gm/cc	Permeability C.G.S. units	Cold crushing strength kg/sq cm	P.C.E. Orton cone	Th. Conductivity B.T.U/hr/sq. ft/in. F.	Th. Conductivity Mean temp. °F.	% Reheat change at C 850 (24 hr)	1250 (24 hr)	1500 (3 hr)	1500 (24 hr)	Ref. underload of 10 lb/sq in Ta C	Te C	L.O.I.	Chemical Analysis % SiO₂	Al_2O_3	Fe_2O_3	TiO_3	CaO	MgO	Alkalies
1.	79	0·58	0·55	11·11	9–10	0·85	500	0·91	—	—	—	940	1150	8·50	31·17	12·58	6·23	0·79	27·85	12·53	0·35
2.	71	0·84	0·56	8·16	9–10	0·90	500	0.10	—	—	—	980	1145	1·09	53·47	33·60	5·93	0·47	1·40	1·99	1·75
3.	77	0·61	0·85	6·89	28–29	1·88	500	0·37	3·9	25·96	—	1075	1315	0·72	50·99	36·84	2·18	0·35	3·87	2·19	2·80
4.	73	0·72	0·96	37·19	31–32	3·10	700	0·3	0·65	13.59	—	1145	1430	0·46	51·86	35·94	2·56	0·86	2·37	2·35	3·10
5.	65	0·94	1·07	22·57	28	2·57	700	0·17	0·70	21·48	—	1100	1340	0·54	53·22	34·96	3·97	1·44	2·64	2·65	0·58
6.	67	0·94	0·41	13·71	30–31	3·00	700	–	0·14	4·4	6·84	1345	1550	0·23	53·88	37·01	3·96	3·17	1·74	0·82	Nil
7.	65	0·97	0·76	9·21	32–33	2·90	700	0·04	0·12	5·12	—	1250	1570	0·32	64·21	30·38	2·40	Trace	1·85	1·64	Nil
8.	66	0·90	0·61	16·38	27–28	3·38	700	0·08	0·20	20·5	—	1360	1490	0·58	67·10	25·57	1·04	1·5	1·75	2·13	0·33
9.	71	0·78	0·14	17·58	31–32	2·29	700	1·25	0·76	—	—	1100	1460	0·68	51·62	40·57	3·87	0·22	1·62	1·44	Nil
10.	72	0·75	1·48	17·72	34–35	2·10	700	0·20	0·22	—	3·14	1435	1630	0·72	52·28	43·00	1·62	0·15	1·56	0·72	Nil
11.	74	0·68	0·92	18·00	18–19	2·56	700	0·19	0·20	Melted	—	1260	1290	0·50	73·13	3·67	1·56	Trace	20·18	1·69	Nil
12.	59	0·97	0·46	37·69	27–28	3·16	700	0·03	0·05	—	0·07	1580	1650	0·44	90·18	2·37	1·15	Trace	4.06	2·39	Nil
13.	43	1·52	0·18	125·71	30–31	5·50	700	—	0·05	7·4	—	1380	1590	0·49	60·77	31·66	2·21	2·17	1·60	1·16	Nil

Low temperature hot-face insulation (Type II IS 2042-1963)

Six samples come under this group and are mainl, made from alumino-silicate raw materials with fireclay as the base. The alumina content varies from 25 to 40%. The P.C.E. varies from cone 27 to cone 33. Porosity of the samples, tested in this group, varies from 65 to 75% and the bulk density from 0·72 to 0·97 gm/cc. The range of the permeability is from 0·14 to 1·07 c.g.s. unit.

The cold crushing strength varies from a low figure of 9·21 kg/sq cm. to as high as 37·19 kg/sq cm. These wide variations in the properties are due to the fact that these insulation refractories were manufactured by different firms using different raw materials, processing techniques, firing temperatures, etc. Due to the large number of variables which affect the thermal conductivity values, it is rather difficult to compare these values and correlate them with other physical properties for the group as a whole. Samples nos. 6, 7 and 8 have a more open texture as seen in Fig. 8 and this has resulted in their comparatively lower crushing strength.

The thermal conductivity values of these samples vary from 2·29 to 3·38 B.T.U./hr/sq ft/inch/°F. It may be observed from the Table that the samples made from alumino-silicate material having 30–40% Al_2O_3 content have thermal conductivity value between 2 and 3 B.T.U. Specimen No. 8 which appears to be made from highly siliceous fireclay, shows a higher thermal conductivity as compared to others. The variation of thermal conductivity with alumina content for insulating bricks of type II is given in Table II.

TABLE II Thermal conductivity vs. alumina content

Type of the brick	Serial No. of the brick	Al_2O_3 %	Thermal conductivity in B.T.U.	Mean temperature F
II of IS 2042-1963	10	43·00	2·1	700
	9	40·57	2·29	700
	6	37·01	3·00	700
	4	35·94	3·10	700
	5	34·96	2·57	700
	7	30·38	2·90	700
	8	25·57	3·38	700

Though all these samples stood the reheat test at 1250°C, they could not stand the 1500 C test. However, two sample nos. 6 and 7 may be capable of withstanding a higher hot face temperature than 1250°C as indicated by their comparatively low contraction at 1500 C. soaked for 3 hours, and their fairly high refractoriness underload values.

Semi-silica insulating brick

Sample no. 11 appears to be made from a semi-silica type of composition with a high percentage of lime. This has brought down the P.C.E. of the material to cone 18–19 and it is also confirmed by the refractoriness under-load value, where the 'ta' and 'te' are very close to each other, which is normally the case with siliceous materials.

Hot face insulation (Type III)

Silica based sample

One of the samples tested had a silica base with about 4% lime and about 10% total fluxes, which is the only indigenous brick tested at the National Metallurgical Laboratory which withstood the reheat test at 1500 C (24 hours) as specifield for type III insulating brick as per Indian Standard Specification (IS 2042-1963). Consistent with its high crushing strength, it has a fairly low porosity of 59% and high bulk density of 0·97 gm/cc. The refractoriness underload value also confirms that it should be capable of withstanding 1500°C reheat test. The thermal conductivity value of this sample which is 3·16 B.T.U. at 700°F mean temperature may be considered to be well on the lower limit for this class of material. Consistant with its low porosity and high bulk density, it has a more or less compact texture which is also revealed by its high crushing strength.

Imported sample

For purposes of comparison, a well known brand of imported hot-face insulation brick was tested. The results are given in Table 1. The texture of the brick is shown in Fig. 9, sample 10, which has an alumino-silicate base with total fluxes on the low side, being only 4%. This brick is very well made and has high porosity and low bulk density for this class of material and at the same time fairly good crushing strength. As this sample had a contraction of 3% in the reheat test at 1500°C with 24 hours soaking, according to Indian Standard Specification, this sample does not pass the reheat test for insulating bricks of type III. As this standard quality of brick is widely used as a hot face brick even at 1500°C or above, it appears that the reheat test specified for type III hot face insulation brick as per Indian Standards Specification is rather stringent.

Though the indigenous sample no. 9 has nearly the same alumina content as the imported sample ; its porosity, bulk density and cold crushing strength and thermal conductivity are also very close to that of the imported sample, the former does not even pass the reheat test for I. S. type II as its reheat shrinkage is more than 1·5% at 1250°C. This vast difference in quality between the two, may be attributed, primarily, to low temperature firing in the case of indigenous sample, though the high flux content may also be partly responsible.

A kyanite based hot face insulation brick with superior properties comparable to some of the imported hot face insulation bricks has been developed at the National Metallurgical Laboratory and the process is covered by a patent.[3, 4] The salient properties of this product are :

Apparent porosity	60—65%
Cold crushing strength	8·09—17·58 kg/sq cm
Refractoriness underload with 2·0 kg/sq cm.	'ta'—1 550°C
Al_2O_3 content	58—60%
Mullite content	75—80%

Light weight fire brick

Along with the above samples, a light weight fire brick, which cannot be classified as an insulating brick, was also tested. As should be expected, its thermal conductivity value was high (5·50 B.T.U. at 700 F mean temperature) and other physical properties like, porosity, bulk density, crushing strength and refractoriness underload were more akin to that of a medium heat duty firebrick.

From Figs. 4, 5 and 6, showing the thermal conductivity of insulating bricks at different temperatures, it may be observed that some of the samples show an increase in thermal conductivity with rise in temperature while others show a tendency in the reverse direction and in a few cases the thermal conductivity is practically the same at all mean temperatures.

Summary and conclusions

In the present study, as the bricks have been collected from different sources and as there are too many variables involved, it is not possible to attribute any specific reason for the particular nature of the thermal conductivity curve, rising with temperature or falling with temperature etc., from the data available. However, these figures will give an idea of the insulating properties of these bricks at different temperatures.

Due to the large number of variables involved, though it is not possible to draw any specific conclusion, it appears probable that in the case of backing insulation the thermal conductivity increases with alumina content, whereas in type II insulation brick the reverse trend is noticed.

From this comparative study of indigenous samples, it appears that there are a few samples especially 6, 7 and 8 which could be classified as superior to type II. But unlike American and other classifications for insulation refractories, we have no other suitable classification into which these bricks fit in.

Amongst the indigenous bricks studied there is only one silica based sample which conforms to type III of I.S. 2042—1963.

Acknowledgement

The authors wish to express their thanks to all the Refractory manufacturers who have supplied the samples and to the Indian Standards Institution for initiating the work and arranging for the samples. Thanks are also due to Shri D. V. Raman for chemical analysis and to Dr B. R. Nijhawan, Director, National Metallurgical Laboratory for his keen interest in the work.

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Development of Aqueous Non-Sludge Forming Zinc Phosphate Bath

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Most phosphating baths are sludge forming which makes handling of the solution and operation of the bath difficult. In recent years, non-sludge forming baths have been developed although their applications have not been extensive.

In this investigation, non-sludge forming zinc phosphate bath has been examined. Various experiments carried out to study the characteristics of phosphate coatings, e.g., coating composition, protective properties etc., using both sludge and non-sludge forming solutions have been outlined. Addition of non-sludge forming compounds, effectively checked sludge formation and gave a good phosphate coating comparable to that obtained from the conventional zinc phosphate bath.

AMONGST various methods of surface protection, phosphating of steel has received much attention. Apart from the self-rust proofing characteristic of the phosphate coating, it offers a good base for painting and other surface treatment and also aids in the lubrication of the rubbing surfaces. The coating is normally crystalline and consists of a mixture of phosphates of iron, zinc or manganese depending on the nature of the salts used in the process. Phosphatising baths usually consist of acid salts of zinc or manganese or both along with other constituents; the composition of the bath is so maintained that the solubility product of secondary and tertiary products is not quite exceeded. When a metal surface is dipped in such a 'balanced' solution, there is a decrease in the hydrogen ion concentration at the metal-solution interface due to acid attack on the metal, which causes the solubility product of secondary and tertiary phosphate to exceed at the metal-solution interface resulting in their precipitation on metal base. Selection of a particular solution composition, operating temperature, etc. is generally made on the basis of the mode of application to be employed, such as, dipping, spraying, brushing, etc. Characteristics such as hardness, porosity, fineness, PO_4 and moisture content of the coating determine performance of the coating under specific service conditions.

There are various proprietary phosphatising processes in use; however technical data on bath composition are scanty. Most phosphatising baths are sludge forming, precipitating secondary and tertiary iron phosphates, which results in the impregnation of ferrous phosphate into the coating, thus lowering corrosion resistance of the coating. The heavy precipitate settles on the hot surface of the tank and the heating coil and forms a hard deposit which is not only difficult to remove, but also forms an insulation barrier for heating the solution. The resulting drop in the bath temperature hinders the formation of the coating, affects its grain size and corrosion resistance properties. Moreover, the precipitate impedes the spray phosphatising process due to the chocking of the spraying nozzles. Elimination of such precipitation from the bulk of the phosphatising solution is, therefore, important. This investigation was taken up to develop a non-sludge forming phosphatising bath. The addition of non-sludge former was investigated in relation to bath composition, its protective properties etc.; phosphate coating obtained from baths containing zinc salts and phosphoric acid without the addition of non-sludge forming compound was also examined.

Experimental procedure

Bath composition

Zinc oxide and phosphoric acid of C.P. grade were used for the preparation of the bath. Two bath compositions A and B were used in this investigation. The zinc and phosphoric acid content of both the baths were similar except that the bath B contained non-sludge forming compound.

Preparation of the samples

Samples of 2·5 × 7·5 cm size were cut from a 3 mm thick hot rolled mild steel sheet. The mill scale was removed by pickling in an inhibited sulphuric acid bath. The surface was prepared by grinding followed by polishing up to '0' emery fiinish. The prepared surface was degreased by rubbing with MgO paste, washed in runing water and then dried.

Phosphatising process

Phosphate treatments were carried out at a temperature of 80°C which was maintained throughout. Bottom heating was found to be inconvenient in the case of sludge forming bath due to heavy precipitate formed during phosphating. Arrangements were, therefore, made for heating the solution in a beaker immersed in a glycerine bath heated to the required temperature. A schematic diagram, illustrating the thermostatic arrangements and the phosphating process is shown in Fig. 1. After the solution attained the desired temperature, samples were immersed in the hot phosphatising solution for the treatment. The samples were treated for 5, 10, 20 and 40 minutes. In each one litre of fresh solution four samples were treated. Samples after phosphatising were washed under running cold water for 2 minutes followed by a dip in hot water for one minute.

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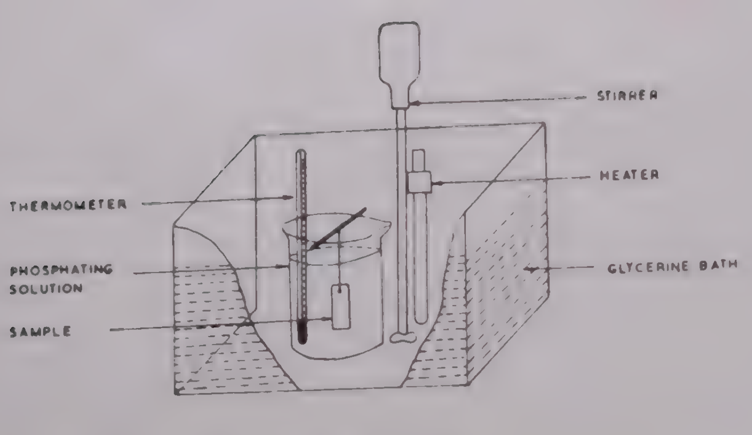


1 *Set up for phosphatising treatment*

The phosphate coating itself does not possess much corrosion resistance properties. Generally some passivating treatment or impregnation with sealing agents, such as oil, grease, wax, etc. are carried out to improve the corrosion resistance properties. Amongst various passivation treatments, dip in 0·1% Cr_20_3 solution is most effective.[2] It was used in the present work. All samples after phosphating, were treated in 0·1% Cr_20_3 solution at 70°C for one minute. Samples for corrosion tests were also treated in oil and lanolin solution. Details of treatment given are furnished below :

Treatment in inhibited oil

Samples were dipped for one minute in a thin lubricating oil to which oleic acid was added as inhibitor. The samples after dipping were kept suspended for 24 hours to drain off excess oil from the surface. The difference in weight before and after the treatment, determined the amount of oil retained by the coating.

Lanolin treatment

Twenty percent solution of lanolin was made in kerosene oil. Phosphatised samples were dipped in this solution for one minute and allowed to dry for 24 hours. The weight of the lanolin film on the surface was determined from the increase in weight of the sample after the treatment.

Determination of weight of the phosphate coating and the extent of acid attack on the base metal during the process of phosphatising

The weight of the phosphate coating and the extent of acid attack of the steel during the process of phosphatising were determined by weighing the test specimen at three different stages, viz. before phosphatising, after phosphatising and after stripping of the phosphate coating in inhibited acid. If W_1 is the weight of the samples before phosphatising, W_2 the weight after phosphatising and W_3 the weight after the stripping of the coating, then (W_2-W_3) would represent the weight of phosphate coating and (W_1-W_3) the extent of acid attack. 15% sulphuric acid solution containing 0·5 gm/l of di-o-tolyl-thiourea was used as the stripping solution. Aggresiveness of this solution on steel was checked by putting a bare steel sample for the time required for stripping off the phosphate coating and negligible attack on steel surface was noted. After stripping, the sample was thoroughly washed in running water and then dried.

Analysis of the phosphate coating

The analysis of the iron content of the phosphate coating was carried out by the standard volumetric method. The samples for iron analysis were obtained by light scrapping with a sharp and hard steel blade.

The PO_4 content of the coating was determined colourimetrically by dissolving the phosphate coating in HCl solution and using ammonium molybdate and hydroquinone. The procedure for analysis as followed by Preston et al[3] was adopted.

Moisture content

Samples in duplicate were weighed after phosphatising and then kept in an air oven at 110°C for 2 hours. These were cooled in a dessicator and reweighed ; difference in weight between the two gave the weight of moisture present.

Spot tests for discrimination of phosphate coatings

The crystalline nature of the phosphate coating indicated that the coating in general, was porous. The degree of porosity depended on the fineness of the crystal and thickness of the deposit. Further, the protective value of the phosphate coating is directly related to its porosity. If the coating is thicker and less porous, it can offer greater resistance to corrosion. For discriminating the phosphate coatings Akimov and Ulyanov[4] have suggested spot test using acidified copper sulphate-sodium chloride solution, which in a modified form, as suggested by Andrew et al[5] and stated hereinafter was adopted in this investigation. Circles of about 1 cm dia. were drawn over the surface to be tested by means of wax pencil. Test solution containing 10% $CuSO_4$, $5H_20$—40 ml, 10% NaCl—20 ml, 1% HCl—1 ml and water 180 ml was applied in drops on the circles, left for one minute and then washed off with water. The surface was dried by means of filter paper and examined for copper colour and was taken to be a measure of discrimination of the phosphate coating.

Corrosion test

The corrosion resistance properties of phosphatised samples after treatment in inhibited oil or lanolin solution were studied by performing salt water droplet test[6] and salt spray test.[7]

(a) *Salt water droplet test :* Solution containing sodium chloride-23.01 gm/l, sodium sulphate-8.9 gm/l, magnesium chloride-9.8 gm/l and calcium chloride-1.2 gm/l was sprayed on the samples so that the suface was covered with fine droplets. With such blanket of salt water droplets, the samples were exposed over a layer of water in a closed dessicator. The samples were sprayed with the salt solution once in a day. Salt droplet tests were continued till the breakdown of the coating was indicated by the apperarance of the rust spots. Nature of failure of the posphatised samples was compared against a standard chart.[8] Details of the standard chart have been shown Fig. 4.

(b) *Salt spray test :* Phosphatised sample treated in oil and lanolin solutions were exposed in the salt spray chamber. The samples were daily sprayed with 5% sodium chloride solution for 8 hours ; for rest of the period these were kept inside the chamber. Tests were continued for 72 hours. Details of the test procedure were followed as ASTM Specn. B 117. Nature and extent of rusting after the completion of the test was compared against the standard chart.

Results and Discussions

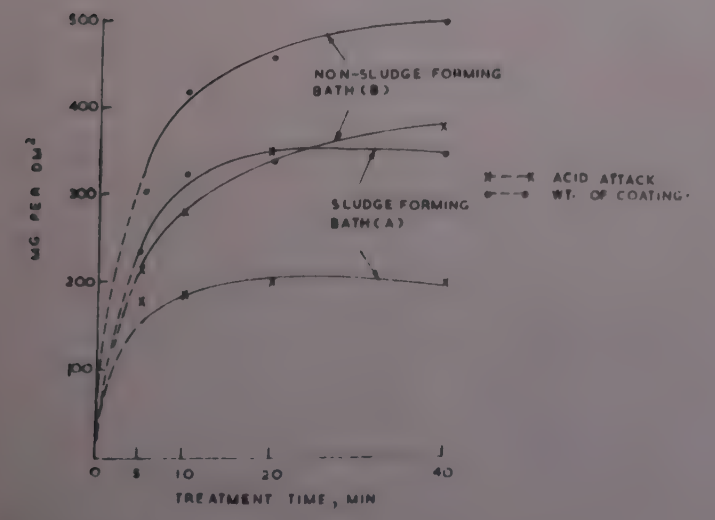
Dense grey, crystalline phosphate coating was obtained from both the baths; the shade of the phosphate coating from the bath B was considerably darker. Phosphatising bath A showed the formation of precipitation. On the other hand, addition of non-sludge former in the bath showed no precipitation or turbidities even after prolonged use.

Weight of the phosphate coating formed and loss of the metal due to acid attack of the samples during phosphating have been plotted in Fig. 2. It is evident from the figure that when non-sludge former was added in the bath, less of the metal due to acid attack and weight of phosphate coating showed higher values probably because of the acidic nature of the non-sludge former, which increased the rate of attack and thereby accelerated the rate of coating formation.

Composition of the phosphate coating

The results on analytical data for PO_4 and iron content of the coating are presented in Table I which reveal no marked variations both in PO_4 and Fe contents of the coating with treatment time. The nature of the coating was also examined by X-ray diffraction technique. For this study, the coating was lightly scrapped and was examined in a 11·46 cm powder camera in Cuk$_\alpha$ radiation using Ievenis and Stramaunis mounting. The X-ray tube rating were 30 KV and 20 mA and exposure of 30 hours was required.

The X-ray powder diffraction pattern obtained is shown in Fig. 3. The 'd' values of different lines were calculated and compared with standard A.S.T.M. values of various probable compounds. As evident from Table II the structure of the coating on steel was found to correspond with that of $Zn_3(PO_4)_2, 4H_2O$. In chemical analysis, however, about 13—15% iron was obtained but the presence of free iron or $Fe_3(PO_4)_2$ in the coating was not detected in X-ray diffraction studies. It is, therefore, plausible that equivalent amount of zinc in the lattice of $Zn_3(PO_4)_2, 4H_2O$ (coating) has been replaced by iron, forming combined phosphate of Zn and Fe of chemical formula $(Zn\,Fe)_3\,(PO_4)_2, 4H_2O$. Assuming the zinc phosphate coating to consist of $Zn_3\,(PO_4)_2, 4H_2O$ and $(ZnFe)_3\,(PO_4)_2, 4H_2O$ in the ratio of 1 : 1, the theoretical amount of zinc and water of crystallisation were calculated from the weight of the coating obtained for different time cf treatment. It is interesting to note that when these calculated values for zinc and water of crystallisation are added up to the corresponding values for PO_4 and iron contents obtained by analysis, a value approaching to the coating weight is reached as shown in Table I, which indicates the probable composition of coating as mixture of $Zn_3(PO_4)_2, 4H_2O$ and $(ZnFe)_3(PO_4)_2, 4H_2O$ in the ratio of 1 : 1. It may be mentioned that the deposit obtained by Trillat and Saison[9] from the conventional zinc phosphate bath was shown to be $Zn_3(PO_4)_2, 4H_2O$ and $(ZnFe)_3(PO_4)_2\,4H_2O$.



2 *Coating formation*

TABLE I Composition of the phosphate coating

Analysis of the phosphate coating	With the addition of non-sludge former 5 min	10 min	20 min	40 min	Without addition of non-slude former 5 min	10 min	20 min	40 min
Data obtained on calculation								
Amount of Zn. gm	·030	·057	0·62	·069	·041	·046	·046	·046
Amount of H_2O gm	·011	·021	·029	·026	·015	·016	·01/	·016
Data obtained on analyses								
PO_4 in gm	·034	·062	·074	·058	·041	·043	·040	·035
Fe in gm	·011	·022	·023	·028	·016	·019	·019	·017
Total in gm	·086	·162	·188	·181	·113	·124	·122	·114
Coating wt. in gm	·088	·159	·172	·188	·114	·123	·128	·127

TABLE II X-ray diffraction data of phosphate coating

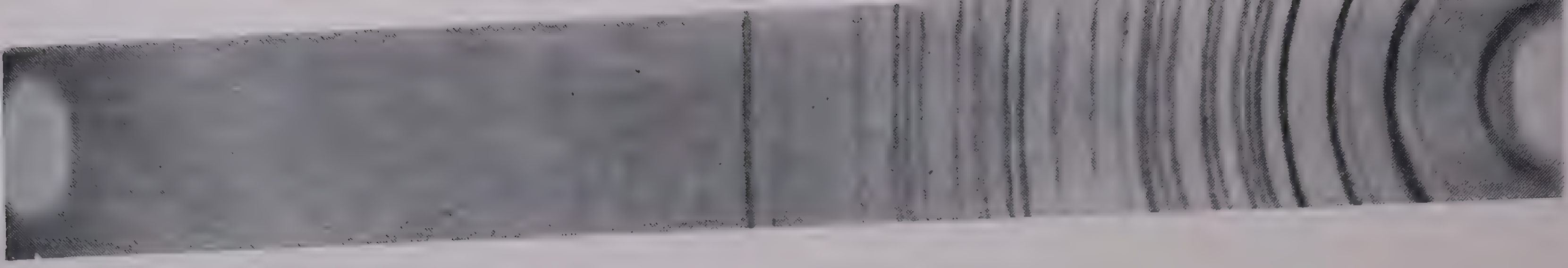
Sl. no.	Intensity	d in Å	d in Å for $Zn_3\,(PO)_2$, $4H_2O$	Intensity I/Io
1.	Strong	8·876	9·1	40
2.	Faint	5·284	5·3	8
3.	V. Strong	4·478	—	—
4.	Faint	3·658	3·65	8
5.	Strong	3·388	3·40	40
6.	V. Strong	2·828	2·85	100
7.	Medium strong	2·617	2·93	40
8.	Medium	2·543	2·52	40
9.	Faint	2·450	2·42	20
10.	Medium	2·291	2·27	20
11.	Medium strong	2·227	—	—
12.	Br. F.	2·052	—	—
13.	Faint	1·980	2·00	20
14.	Faint	1·933	1·04	35
15.	Medium faint	1·903	—	—
16.	Faint	1·832	1·82	30
17.	V. Faint	1·820	—	—
18.	V.V. Faint	1·780	1·78	4
19.	,,	1·722	1·75	8
20.	,,	1·696	1·70	10
21.	,	1·673	1·67	4
22.	,,	1·639	1·63	4
23.	,,	1·619	—	—
24.	,,	1·602	1·59	4
25.	,,	1·564	1·56	12
26.	,,	1·5,7	—	—
27.	Faint	1·524	1·52	14
28.	,,	1·489	1·48	2
29.	V.V. Faint	1·460	—	—
30.	V. Faint	1·448	1·44	8
31.	,,	1·427	—	—
32.	,,	1·415	1·41	8
33.	V.V. Faint	1·381	—	—
34.	V. Faint	1·211	1·30	4
35.	,,	1·287	—	—
36.	,,	1·267	1·27	6
37.	,,	1·209	—	—

Moisture content

Practically no difference in weight of the phosphatised samples before and after drying at 110°C was observed which showed absence of entrapped moisture in the coatings.

Absorption of oil and Lanolin solution

In Table III weight of the oil and lanolin film retained on the phosphatised samples have been compared. It will



3 *X-ray diffraction pattern of the phosphate coating*

TABLE III **Weight of oil and lanolin film retained by phosphate coating**

Bath	Time of Treatments in minutes	Wt. of the Coating in gm/dm²	Wt. of the oil film gm/dm²	Wt. of the Lanolin film gm/dm²
Non-Sludge forming Bath B	5	·2335	·081	·039
	10	·423	·069	·034
	20	·459	·071	·037
	40	·5018	·072	·032
Sludge forming Bath A	5	·3048	·079	·040
	10	·3272	·106	·034
	20	·3420	·098	·042
	40	·3381	·1132	·037

TABLE IV **Results on spot test**

Bath	Time of treat-ment in min.	Appearance of copper spot after ½ min.	1 min.	2 min.	3 min.	4 min.	5 min.
Non-Sludge forming Bath B	5	Faint	Definite				
	10	Nil	Trace	Faint	Definite		
	20	Nil	Nil	Nil	Trace	Faint	Definite
	40	Nil	Nil	Nil	Nil	Nil	Faint
Sludge forming Bath A	5	Trace	Faint	Definite			
	10	Nil	Faint	,,			
	20	Faint	Definite				
	40	Trace	Faint	,,			

be evident from the table that the amount of oil or lanolin solution retained on the surface is related to the weight of the phosphate coating.

Spot test

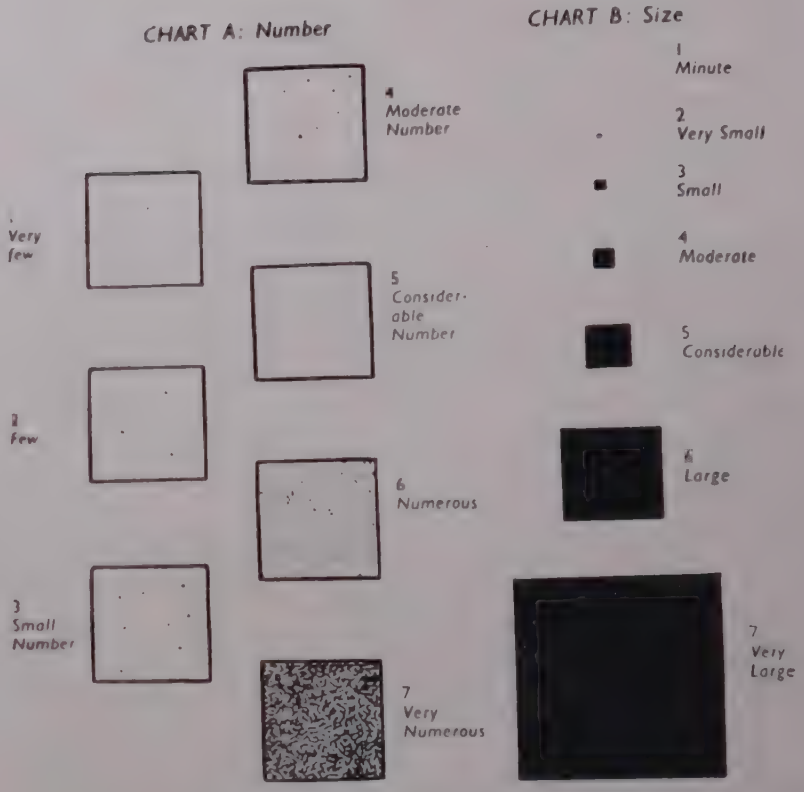
Results on spot tests have been shown in Table IV. No definite copper colour developed on the spot in less than one minute.

Salt droplet test

In salt droptet tests, several rust spots were found to develop on the surface of the phosphatised samples. The extent and intensity of attack has been compared in Table V against a standard chart. It will be evident from Table V that samples with heavy phosphated coating showed superior protection. It is also evident from the Table that the treatment for 10 minutes was sufficient for maximum protection.

Salt spray test

Salt spray test on the phosphated samples was continued for three days with 8 hours spray treatment and for the rest of the time the samples were kept inside salt spray chamber without using the spray itself. No rust spot was visually observed on the samples upto the exposure period of 48 hours. In Table VII comparative results after 72 hours have been shown. It will be apparent from the above Table that the protectiveness of the phosphate coating obtained from both sludge and non-sludge forming bath is not markedly different.



4 *Standard chart for examination of the ru:t spots*

TABLE V **Results on salt droplet test**

Bath	Time of treat-ment min.	Characteristics of the rust spot dsveloped: After treated in inhibited oil: No. of rust spots (Chart A)	Size of rust spots (Chart B)	After treated in Lanolin solution: No. of the rust spots (Chapter A)	Size of the rust spots (Chart B)
Non-sludge forming Bath B	5	2	3	2	2
	10	1	4	1	1
	20	2	3	1	1
	40	1	3	2	1
Sludge forming Bath A	5	1	4	2	4
	10	1	3	2	2
	20	1	2	1	4
	40	Nil	—	2	4

TABRE VI Details of the standard chart shown in Fig. 4

Decsriptive number.	Number—Chart A Std. term.	No. per sq dm.	Size—Chart B Std. term.	Area sq. cm
1	Very few	33	Minute	·0006
2	Few	100	Very small	·003
3	Small number	330	Small	·016
4	Moderate No.	1000	Moderate	·08
5	Considerable No.	3300	Considerable	·4
6	Numerous number	10000	Large	2·0
7	Very numerous Number.	33000	Very large	10·0

TABLE VII Results on salt spray test

		Characteristics of the rust spots developed			
		After treated in inhibited oil		After treated in lanolin solution	
Bath	Time of treatment min.	No. of the rust spots (Chart A)	Size of the rust spots (Chart B)	No. of the rust spots (Chart A)	Size of the rust spots (Chart B)
Non-Sludge forming Bath B	5	Nil	—	1	3
	10	Nil	—	Nil	—
	20	Nil	—	Nil	—
	40	Nil	—	Nil	—
Sludge forming Bath A	5	1	3	Nil	—
	10	1	2	Nil	—
	20	Nil	—	Nil	—
	40	Nil	—	Nil	—

Summary

1. Non-sludge forming bath could be successfully developed by adding a non-sludge forming compound.
2. Addition of non-sludge forming compound does not alter the coating composition.
3. Protectiveness of the zinc phosphate coating obtained from the bath containing non-sludge former is as efficient as that obtained from the ordinary zinc phosphate bath.
4. Phosphating for ten minutes is sufficient to offer maximum protection.

Acknowledgement

The author's thanks are due to Dr T. Banerjee, for his helpful guidance during this investigation and also to Dr B. R. Nijhawan, Director, National Metallurgical Laboratory for his valuable suggestions and keen interest.

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Shri Jawaharlal Nehru–Builder of Modern India

'............If any people choose to think of me then, I should like them to say: This was a man who with all his mind and heart, loved India and the Indian people. And they, in turn, were indulgent to him and gave of their love most abundantly and extravagantly...........'

SHRI Jawaharlal Nehru is no more and yet he has been immortalized. He was a lover of science, believed intensely in Indian scientific research and technology and its undisputed role in achieving a dynamic pattern of social and economic progress in our country. Modern science fascinated him. To Shri Jawaharlal Nehru, the role of modern science in building the modern India was supreme, unchallenged and yet challenging —a case of sincere conviction and not merely a belief. Shri Jawaharlal had said a decade before India achieved independence that,

> '..............It is Science alone that could solve the problems of hunger and poverty, of insanitation and illiteracy, of superstition and deadening custom and tradition, of vast resources running to waste, of a rich country inhabited by starving people...........who indeed could afford to ignore Science today ? At every turn we have to seek its aid..............the future belongs to Science and to those who make friends with Science...........'
>
> 'Every Institute of Science, every Laboratory, every University, where science is nurtured should become the true temple for the search of truth and for the advancement of our people and of humanity...............'

Dr B. R. Nijhawan, Director, National Metallurgical Laboratory explaining to Shri Jawaharlal Nehru some of the products and processes developed at the National Metallurgical Laboratory. Sir Jehangir Ghandy, Chairman, Executive Council, National Metallurgical Laboratory and Mr J. R. D. Tata, Chairmam, Tata Industries Ltd, accompanied Shri Nehru.

Mrs B. R. Nijhawan extending a warm welcome to Shri Jawaharlal Nehru at the National Metallurgical Laboratory.

The establishment of a chain of National Research Laboratories, soon after independence was to Shri Jawaharlal Nehru, pattern of progress, a dream fulfilled and a path to follow. At the opening of the National Metallurgical Laboratory in November, 1950, Shri Jawaharlal Nehru said

> '..............I do believe that there can be no real progress either in this country or in any other part of the world without its being founded and based on science, on the scientific application to many things in life and if I may say further, on the scientific temper of the mind of people. And the last perhaps is as important as any other, because, science represents, I hope, not only the devoted study of a particular subject, the devoted search for truth but in the process it produces a dispassionate mind. It makes the person study objec-

Shri Jawaharlal Nehru and Dr Zakir Hussain, Vice-President of India, are keenly observing the products developed at the National Metallurgical Laboratory which are explained by Dr B. R. Nijhawan, the Director of the Laboratory.

> tively, it prevents an individual or a group being swept away by momentary passion and it rejects anything that it considers wrong or untruthful mercilessly...............'

Visiting again in March, 1958, Shri Jawaharlal Nehru commended the work of the National Metallurgical Laboratory and urged earliest utilization of potential research results in all possible practical fields without waiting to find out who should make use of them. In his appreciative address to the staff of the National Metallurgical Laboratory, he said :

> '...............It is now eight years since I came here when this laboratory was opened and on coming here now, I oberved many dynamic developments, many more improvements and new processes. Even before coming here I have heard about the new processes developed in this Laboratory, especially of the new stainless steel which has received a great fame and appreciation both in India and abroad. It is with this inspiration that most of the scienitfic workers responded most magically to the challenge thrown by the backwardness of our country and this has created in us an indefatigable zeal for work. ....'

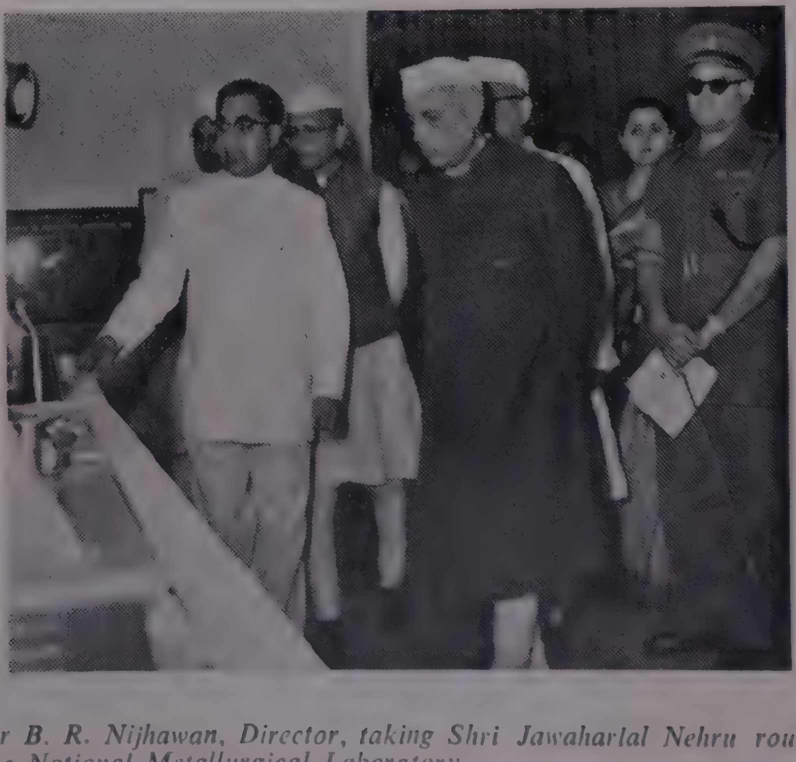
Shri Jawaharlal Nehru discussing the work of the National Metallurgical Laboratory with Dr B. R. Nijhawan, Director of the Laboratory.

> '..............One thing I always fear is that when any good work is done and good processes developed in our laboratories, these get stuck up and it becomes rather difficult to derive proper benefits out of them. A long time elapses and industrial exploitation of such processes is postponed and we feel that we have attained the goal or with that our responsibility ends. This is not right. When outstanding processes are developed, we should make use of them at the earliest and not wait to find out as to who should make use of them. As these are useful, Government itself should use and benefit from these processes ....'
>
> '......... . With due regard to the excellent work that is being done in this Laboratory, I extend my hearty congratulations to your Director and to you...........'

Nehru's India, India of flowing rivers, matching powerful dams, India of science and industry, India of truth and non-violence, India of ancient glory and new visions, Indian's India—a land of freedom and independence—this India of ours is enshrined in Tagore's Gitanjali.

> 'Where the mind is without fear and the head is held high ;
> Where knowledge is free ;
> Where the world has not been broken up into fragments by narrow domestic walls ;
> Where words come out from the depth of truth ;
> Where tireless striving stretches its arms towards perfection ;
> Where the clear stream of reason has not lost its way into the dreary desert sand of dead habit ;
> Where the mind is led forward by thee into ever-widening thought and action—
> Into that heaven of freedom, my Father, let my country awake'.

With the passing away of Shri Jawaharlal Nehru the memorable light is out and yet the light in memorium is immortal, guiding us, leading us on to feel the strength and true pride of being Indians and in dedicating ourselves to the task of building our India, Nehru's India



Dr B. R. Nijhawan, Director, taking Shri Jawaharlal Nehru round the National Metallurgical Laboratory.

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Notes and new

HOME NEWS

US, UK consortium aid for 5th state steel plant

The Anglo-US steel consortium is understood to have agreed in principle to assist the Union Government in setting up the fifth State steel project. The offer of the consortium is 'to aid and construct' the project with full association of Indian engineering and construction skill and maximum utilisation of indigenous equipment and materials. The consortium will submit its recommendations on the choice of the site in near future. The intention is that the consortium will review and analyse the existing reports on Goa-Hospet, Billadila–Visakhapatnam and Salem–Neyveli. It has been agreed that the consortium will proceed with detailed project study only after the Union Government has indicated the site.

Hindustan Times, 11.10.1964.

Russia given sole technical control over Bokaro steel plant

The Russian Government wants to have undivided technical responsibility for the Bokaro steel plant project which, it is convinced, is inspired by the Russian Government's desire to give its best in both designing and engineering services. Designing of the various equipment needed for the plant has been started by over 100 consultants and engineering units in the USSR under the supervision of Dipromes (Central Design Institute for Metallurgical Plant). The project report will be the cumulative work of these units. The Soviet Government is expected to submit the project report to the Union Steel Ministry by the end of June, 1965. The USSR has agreed to the maximum use of the equipment manufacturing capacity in India and to the association of Indian engineers with the construction work. It will incorporate in its designing programme India's standard units. The estimated total cost of the plant will be known only when the project report is ready.

Statesman, 11.10.1964.

Tinning plant in Rourkela—first in Asia

The first electrolytic tinning plant on the Asian continent is to be erected in the Rourkeia iron and steelworks in India. After Demag already received the order for supplying the first stage of expansion last year, this same company has now received an order for supplying machinery and plant for the second phase of expansion together with the main order. When the plant is commissioned it will have an anual capacity of 150,000 tons of tin plate and will thus be among the largest of its type in the world. India will then be able to produce and process more tinplate.

Hindusthan Standard, 12.10.1964.

Copper production under Fourth Plan

Four projects to produce about 58,000 tonnes of copper in the Fourth Plan period have been taken up for detailed investigations by the Geological Survey of India and the Indian Bureau of Mines. These are likely to cost about Rs.39 crores. The step has been taken by the Ministry of Steel and Mines in order to meet the demand in the next plan. According to present estimates, the requirements of copper are expected to rise to 250 000 tonnes by the end of the Fourth Plan, compared with 138 000 tonnes by the end of the current plan.

The schemes which include an integrated copper project to produce 15 000 tonnes of metal in the Rakha-Roam-Siddeswar blocks in the Singhbhum district of Bihar, where copper mineralisation is promising, is at present being investigated by the Geological Survey of India and the Indian Bureau of Mines. According to present indications, the deposits in this area will sustain a metal production of the order of 15 000 tonnes, and it is hoped that a project to produce this quantity of copper metal can be commissioned before the end of the next plan. Another project to produce 10 000 tonnes of copper from Kolihan, where deposits of copper are also promising, is presently being investigated by the Indian Bureau of Mines. The project is close to the Khetri deposits in Rajasthan. According to present indications, the deposits will be able to sustain metal production of the order of 10 000 tonnes a year. The scheme is exected to materialise by about the middle of the Fourth Plan. It has been estimated that the Kolihan project, up to the stage of producing concentrates, will involve a capital expenditure of Rs 10 crores.

A project to produce to 2 000 tonnes to 3 000 tonnes of copper from the Guntur district of Andhra Pradesh is also being investigated by the Geological Survey of India and the Indian Bureau of Mines. The present indications are that two or three of these deposits can be proved by about the middle of the next plan and each may sustain metal production of the order of about 2 000 tonnes to 3 000 tonnes. Each of the deposits is likely to be small in size but of a relatively high grade. For the exploration of these projects, a tentative provision of Rs 1 crore is being made in the next plan. A project to set up a smelter of 30 000 tonnes capacity, based on imported concentrates, is to be exploited with technical as well as financial collaboration with foreign parties owning or controlling overseas mineral deposits. The project is estimated to cost about Rs 8 crores. Such a smelter can be used wherever concentrates can be produced indigenously. A feasibility report on this is being prepared.

Journal of Mines, Metals and Fuels, XII (9), 1964.

Plans for zinc

The demand for zinc at the end of the Fourth Plan is expected to be 225 000 tonnes, compared with 136 000 tonnes at the end the of Third Plan according to the latest estimates prepared by the Ministry of Steel and Mines. To meet the enhanced estimated requirements, the Ministry of Mines has drawn up various projects where investigation, research and pilot plant tests are necessary to prove reserves. These projects, when fully implemented, will go a long way in meeting additional requirements. These are estimated to cost about Rs 72 corres.

A project to set up a zinc smelter with a capacity of 30 000 tonnes, based on imported concentrates, and with Polish collaboration, has been finalised. The project is expected to cost about Rs 12 crores, which will mostly be incurred during the Fourth Plan Period. Another project is for the development of the Zawar zinc deposit in Rajasthan to yield about 50 000 tonnes of metal a year. At present, the Zawar zinc deposits are being developed to yield about 18 000 tonnes of metal a year. The establishment of two more zinc smelters of 50 000 tonnes capacity each, based on imported concentrates, has also been found to be feasible.

Journal of Mines, Metals and Fuels, XII (9), 1964.

Korba aluminium project

Talks on setting up an integrated aluminium project at Korba in Madhya Pradesh have started between the Hungarian team of experts and the Government of India. The project will have a capacity of 120 000 tonnes of alumina and 30 000 tons of aluminium metal per annum supported by facilities to manufacture aluminium semis. The demand for aluminium by the end of the Fourth Plan is expected to be about 260 000 tonnes. This demand is proposed to be met by the expansion of the existing aluminium units and with the establishment of new units.

Times of India, 9.10.64.

Uranium position in India flourishing while world's reserve dwindling

While the world's reserves of uranium—the source of all atomic energy—are dwindling, India's position in regard to uranium is very satisfactory. The Atomic Energy Commission's assessment in this respect is based on the fact that in recent years large deposits of monazite have been found on the Bengal-Bihar boarder and substantial uranium deposits in Bihar. Even with its proved uranium reserves, India is today able to support a nuclear power capacity for over nine million kw of electricity. The production of nuclear power envisaged by the end of the Fifth Plan is, however, only three million kW.

One of the uranium deposits in Bihar is being developed industrially and a uranium mine is being opened in the area. A uranium mill with a capacity of 1000 tonnes of ore per day and with provision for future expansion is also being set up at Jaduguda near Jamshedpur at an estimated cost of about Rs 4·29 crores. The mill has been designed by Indian scientists and engineers and is being installed without any foreign technical assistance.

Hindusthan Standard, 23.10.1964.

Three new coal washeries to start production by 1966

Three coal washeries with a total capacity of more than six million tonnes a year are expected to go into production almost simultaneously in March 1966. Three other projects for coal washeries are at various stages of negotiation. They are likely to be commissioned towards the close of the Fourth Plan. The plan to develop deep mining in collaboration with the United States, The Soviet Union, Poland, France and the United Kingdom, which is linked with the coal washeries programme, is now likely to be modified in view of the reappraisal of the demand for non-coking coal.

Hindustan Times, 8.10.1964.

New plant to produce heavy duty bricks

The National Buildings Organisation, Ministry of Works and Housing, is taking steps for the establishment of an integrated plant for the production of facing bricks, heavy duty bricks and vitreous clay tiles. The proposed plant will have a capacity of producing 2·5 million sq ft vitreous clay tiles per year from clays of the Indo-Gangetic plain. The capital investment required will be Rs 850 000. The foreign exchange component of which will be about Rs 50 000 oniy.

Indian Express, 19.10.1964.

OVERSEAS DIARY

Japanese steel industries

Mr Shigeo Nagano, President of the Iron and Steel Federation of Japan, has stated that one of the most important reason for the astounding resurgence of the Japanese steel industry is the establishment of coastal steel plants. These enjoy six main advantages over inland plants. These is an increasing dependence on imported iron ore; enormous reserves of excellent iron ore are being developed in various parts of the world; large ore carriers have lowered transportation costs; there has been a relative decline in the proportion of coal used; where coal is still used it can be imported very cheaply and heavy oil, which is increasingly in use, can also be landed cheaply. In steel production, Japan has overtaken France in 1959, Britain in 1961 and West Germany in the fiscal year ending March, 1964. At 34·1 million tons, its crude out put made it the world's third largest steel producer, after the US and the USSR.

This remarkable progress reflected the high growth rate of the whole Japanese economy, especially in such steel using industries as construction, shipbuilding, machinery and motor vehicles. The expansion of exports had also played its role. But besides the overall effort which has kept steel manufacturers in the van of Japan's national economic growth and the advantages conferred by coastal steel plants, there were other factors to be noted. One of these was the technological innovation associated with the large scale modernisation of equipment. The destruction arising from the war made it essential for the industry to engage in comprehensive modernisation and expansion programmes. Between 1951, when these were launched, and the end of 1963, some $ 4,000 million had been invested.

As a result of these programmes, the main equipment of the Japanese steel industry had been fully modernized, and since modernization fortunately coincided with the appearence of many technical advances, the latest technology had been fully incorporated into the industry's new plants. In the installation of large blast furnaces, in the wide dissemination of oxygen converters (LD process), and in the capacity and productivity of strip mills, the Japanese steel industry came close to leading the world.

Thus, the Japanese steel industry enjoyed two major advantages—the ideal siting of its plants and the most modern and efficient equipment. By utilizing these two favourable factors to the fullest extent, the industry had not only overcome the handicap of a lack of domestic raw maerials, but had also been able to develop its competitive strength to the point where it was equal if not superior, to that of other major steel industries. This process had been helped by a substantial lowering of production costs including a lowering of the relative consumption of raw materials and fuels. For instance, the amount of coke needed to produce one ton of pig iron in Japan had steadily been lowered from 840 kg (a national average) in 1953 to 520 kg. In comparison the national average in the US in 1963 was 669 kg, in West Germany 719 kg and that in France was 846 kg.

Steel Lines, September 25, 1964.

Britain to be first in Kaldo

While the UK has recently produced its first heat of steel by the Kaldo process, that country is destined to have the world's largest Kaldo basic oxygen steel capacity before the year's end. First on the stream was the Rotherham works of Park Gate Iron and Steel Co. where the Kaldo plant is part of a development scheme that includes an electric melting furnace and rolling facilities. Another plant scheduled to go on stream is that of Shelton Iron and Steel Ltd at Stoke-on-Trent. This steelmaking shop will have two 45-55 ton Kaldo converter and four continuous casting units. A unique steelmaking facility nearing completion is that of Consett Iron Co. with its two 100-ton LD converter and two 100-ton Kaldo vessels. Finally, in the array of new Kaldo facilities for the UK is Stanton Iron Co, where iron is to be refined in a Kaldo furnace of 55-70 ton capacity.

Journal of Metals 16 (15), 1964.

Special steel plant at Sheffield

Europe's most advanced plant for making special steel- The English Steel Corporation's new £26 000 000 plant at Sheffield—has been opened by the Duke of Edinburg. The plant which can produce up to 500 000 ingot tons of carbon and alloy steels a year, will bring large scale production techniques to the manufacture of a high precision product. A complete and closed circuit television are to be used to speed up production. The new works will raise the total annual output of the English Steel Corporation to over 1 000 000 tons.

Journal of Iron and Steel Engineering 4 (2), 1964.

Steel output in Brazil

Brazilian steel output rose to 3·8 m tons last year one million ton more than in 1962. The country's biggest producer was the Companinia Siderurgica Nacional (CSN), with a total output of 1 270 000 tons. An expansion programme, financed by a US loan of $5·5 m is expected to expand CSN capacity by 200 000 tons a year. Iron and Steel production is scheduled to rise to 4 800 000 tons in 1965.

British Steel Maker, 50 (10), 1964.

Aluminium plant in Egypt

Preliminary details of the United Arab Republic (Egypt) Five Year Plan 1965–70, include provision for an aluminium industry. A 40 000 ton aluminium reduction works is to be built either at Aswan or at Alexandria. It would be equipped with furnaces in the 80 000–100 000 A range, and would use imported alumina, petroleum coke and other raw materials. The cost of electric power from the Aswan dam will be very low.

Light Metals 27 (315), 1964.

Huge vacuum brazing furnace

Aerojet-General Corp, Sacramento, California, is installing the world's largest vacuum brazing furnace for processing large rocket engine nozzles. The unit is a bottom loading vertical vacuum furnace, has a maximum operating temperature of 2 300°F and can be operated as a hot or cold walled furnace. The 12 ft diameter by 13 ft high charges area divided into six heating zones, each with a proportion controller and a 250 kW transformer—can handle loads up to 14 000 lb. Maximum operating vacuum of 1 micron mercury is maintained by a pumping system consisting of a three stage oil vapour diffusion pump and two mechanical pumps.

Metal Progress, 85 (6), 1964.

Recent developments

Refining of OH steel in the ladle with synthetic slag

Trials have been undertaken in the USSR with synthetic slag refining of OH steel in the ladle. The synthetic slag used was of the composition—40–41% Al_2O_3 ; 54–56% CaO ; 1·5–2% SiO_2 ; 1–3% MgO and 0·2–0·5% FeO. The sulphur content of such treated steel was then only 0·006–0·012%. The quality of refined low-alloy structural steels, tool steels, low carbon and carbon steels after refining with synthetic slag was better than the quality of the same types of steel manufactured in electric arc furnaces.

Synthetic slag for the purpose was manufactured in electric arc furnace. The best results in the refining of OH steels were achieved in treating steel from 100 and 200 ton OH furnaces. This method is now recommended for use in all steelworks in Soviet Union.

Steel times, October 9, 1964.

Fuel circular converter step forward

Japan's Fuji Iron & Steel Co. has developed a circular converter process that has growth capabilities towards continuous steelmaking operation. The process has its roots in a technique used in Japan during World War II. It was called the 'runner refining process'. Then hot metal was refined blowing air through it while flowing slowly via a runner from the blast furnace through a series of other furnace. The converter, which employs oxygen lances, is based on the runner principle.

Steel, Sept. 14, 1964.

Mould Addition

Claim to produce vastly superior surface on top poured ingots without the necessity of coating the moulds prior to teeming, the latest mould addition from the steelwork division of Foseco Ltd is simply added before teeming commences. Marketed under the name of 'Stelotol 20'. the product is non-toxic and in no way affect the metallurgical qualities of the steel.

A weighed quantity of 2 oz/ton is dropped into the untreated mould and the metal teemed directly on it. It can be applied at any time before tapping and is not dependent on the mould temperature as are many conventional dressings.

Iron & Steel, 37 (9), 1964.

A new high strength weldable aluminium alloy—X7002

A new high strength weldable aluminium alloy—X7002—was developed to meet the growing need for a material with following characteristics : good weldability, ability to be heat treated to relatively high strength levels, resistance to stress corrosion cracking and fatigue, freedom from notch sensitivity, formability and good cryogenic behaviour. The alloy's weldability makes it particularly suitable for aerospace components where material with low density and high strength must be fabricated into complex shapes. Alloy X7002 is a member of the aluminium–zinc–magnesium–copper system and has the nominal composition—3·5% Zn ; 2·5% Mg. and 0·75% Cu. Alloys of this class are the strongest aluminium alloys known.

All fabrication techniques, such as rolling, extrusion and forging are suitable with the alloy. Its cold forming characteristic are excellent in all gauges and tempers, and its composition is compatible with many other alloys to which it can be easily joined by welding.

The standard heat treatment for X7002–consists of soaking at 875°C, cold water quenching, incubating a minimum of four days at room temperature and then ageing 48 hours at 253°C. The bending characteristics of X7002 are comparable to other fully heat treated high strength aluminium alloys, specially in normal plate thickness. The small coper addition in X7002 enhances the resistance to corrosion. It was found that stress corrosion characteristics of X7002 are superior to those of the more familiar aluminium-zinc-manesium alloys such as 7075 and 7079. Weldment in X7002 that are stressed to 75% of yield strength by constant loading in 3·5% sodium chloride (alternate immersion) lasted 66 days before failure—and failure was due to general pitting attack and not stress cracking. Unwelded stressed specimens with a slightly larger cross section lasted a minimum of 89 day, again failing without cracking. Failure within 30 days has been generally accepted as indication of stress corrosion susceptibility.

Alloy X 7002 has an endurance limit superior to that of 2000 series alloys and other alloys in the 7000 series. Extensive test results justify considering X7002 for structure where fatigue strength is an important factor. Alloy X7002 can be welded satisfactorily by the tungsten metal arc, inert gas process.

Metal Progress 86 (1), 1964

Hydrostatic Extrusion—A Technique of Promise

Electron tube technology appears like to benefit from an interesting new production method—hydrostatic extrusion. This process capitalizes on the phenomenon that materials which are ordinarily brittle at room temperature become ductile under high pressure. According to research at the Pressure Technology Corp. of America, metals can be extruded from a chamber filled with fluid at 350 000 psi through a die and into a chamber filled with fluid at a lower pressure. By this process, a 0·150 in diameter billet of TZM molybdenum was reduced to 0·125 in diameter, a 30% reduction in area. Steel, copper alloys, aluminium alloys, magnesium and bismuth have also been extruded by this process, the length of such extrusions being practically unlimited.

Metal Progress, 85 (5), 1964

Longer Life for Mill Rolls

The British Iron & Steel Research Association claim a substantial increase in the life of cold strip mill rolls as a result of plating them with a thin electrolytic deposit of hard chrome. Work trials by Bisra's mechanical working division have shown that a thin (as little as 0·004 in) coating of hard chrome considerably reduces the rate of wear and gives a better and more consistant surface finish to rolled material.

The first trials were carried out on various stainless steel strips. With a 0·0004 in. facing, a five-fold increase in life was obtained while fully maintaining a high quality surface finish. An acceptable surface finish was maintained, in fact, right to the point where the chrome wore through. In another mill, rolling mild steel, one of the conventional rolls was replaced by a chrome plated roll and a direct comparison made. Again a five-fold improvement was obtained.

The trials to-date have been carried out on conventional, reversing and Sendzimer mills rolling mild and stainless steel strips upto 18 in. wide. According to Bisra, there appears to be no reason why similar improvements cannot be expected for wide strip and all grades of steel.

British Steel Maker, XXX (8), 1964.

Hot grinding

Glowing hot billets are now hot ground immediately after their removal from the furnace. Surface inperfections and impurities can be removed from the billets and ingots with skin temperature on excess of 1500°F. In all instances, it can be expected to cut costs and production time. This development, a natural supplement to continuous casting, offers the steel industry the promise of in line processing of metal directly from the furnace to the rolling mill.

In spite of vastly accelerated speed of the stock removal and the extremely high temperature of the working surface, the life of the abrasive wheel is not reduced when measured in terms of metal removed. The entire system including grinding wheel, motor and grinding machine show no adverse effects as a result of the extreme temperatures.

Iron & Steel Engineer, XLI (9), 1964.

A new fatigue testing method

The method has been devised in Plasma Physical Laboratory, Princeton University, USA. In this test, a sample of the material is supported between two electrically insulated terminals in an envelope (of non-magnetic metal or glass) which is evacuated or filled with inert gas. An alternating current is passed through the sample to maintain the desired temperature, and the envelope is positioned so that this heating current, following in the sample, is at right angles to a homogenous magnetic field. Since the current, magnetic field and orientation are known, the force on the sample is known. The temperature can be adjusted conveniently, and the sample can be observed visually during testing. The number of stress cycles per second can be adjusted by changing the frequency of the heating current. Many stress cycles can be achieved in relatively short periods of time. For instance, at a rate of 1000 cycles per sec. the sample would undergo about 10^8 cycles in 24 hr. Due to the number and rapidity with which the stress cycles are applied, a broader experimental domain is available. The necessary equipment is, for the most parts, simple and inexpensive. The volume and intensity of the magnetic field is the major factor determining cost. It is felt that permanent magnets would be suitable in most instances.

Metal Progress 85 (5), 1964.

Melt analysis system

A new optical emission spectrometer combined with a pneumatic tube system for sending samples and analyses, provides closer control of heat quality, shorter furnace operating time and reduced analysis costs at Birdsboro Corpn.

The spectrometer is equipped with digital recording and typewriter readout. It is now set up to record amounts of 11 major and minor elements and is capable of recording 60. The smallest trace now measured is boron at 0·0005 per cent, but the spectrometer will record amounts down to 0.0001 percent, It is calibrated with metal samples from the US Bureau of Standards.

In operation, a sample is removed from the melt and cast. It then travels via pneumatic tube to the laboratory, where it is sectioned and polished. The ground surface is subjected to an electric arc or spark in the spectrometer and the resultant ultraviolet radiation analyzed to determine the amounts of various elements present in the samples. The typewritten analysis is then sent back to the furnace room via the pneumatic tube. This provides a written record and eliminates possible telephone error.

Spectrometer readout takes 1½ min. and the entire cycles, from receipt of the sample to sending results. takes 6–9 min. making it possible to control the entire composition of a melt in progress and control even the major elements in a melt without long furnace operating time.

Iron and Steel Engineer XLI 9, 1964.

Statistics

MINERAL PRODUCTION

Metallic minerals

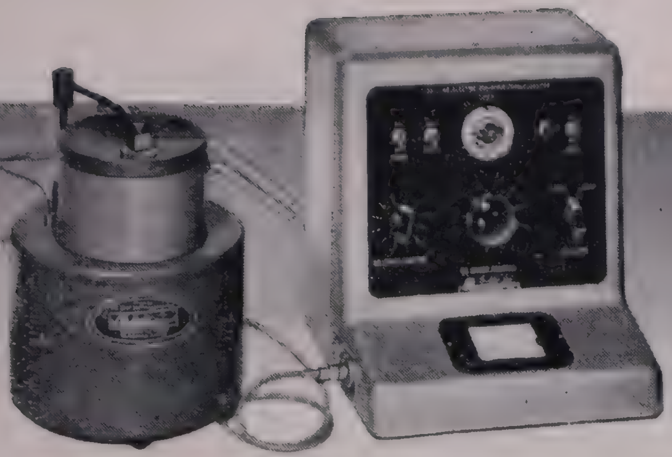
Year		Chromite (tonnes)	Iron ore (000 tonnes)	Manganese ore (000 tonnes)	Bauxite (tonnes)	Copper ore (tonnes)	Gold (kg.)	Ilmenite (tonnes)	Lead concentrates (tonnes)	Zinc concentrates (tonnes)
1960		8 343	890	100	32 282	37 324	416	20 813	520	816
1961		3 827	1 022	102	39 659	35 272	406	14 516	461	771
1962		5 554	1 114	101	47 750	41 000	423	11 500	532	835
1963	July	2 155	1 254	78	44 298	39 590	357	550	461	846
	August	2 205	1 227	82	33 348	37 502	354	541	427	770
	September	1 910	1 202	75	33 999	40 265	343	556	400	826
	October	3 088	1 211	80	32 749	43 029	344	763	325	692
	November	2 917	1 257	90	44 087	40 008	317	948	380	728
	December	1 303	1 229	86	47 806	42 241	346	905	407	897
1964	January	2 165	1 282	80	48 569	35 582	361	722	370	840
	February	2 119	1 262	85	48 141	38 978	350	494	443	867
	March	3 756	1 201	119	49 684	38 315	406	470	475	745
	April	5 697	1 217	104	44 703	41 271	397	524	392	842
	May	5 122	1 180	104	44 682	40 237	348	603	470	818
	June	4 787	1 165	108	43 280	36 685	360	607	641	958
	July	...	1 184	...	...	...	...	...	...	...

Monthly Abstract of Statistics, Vol. 17, No. 10, October, 1964.

Non-metallic minerals

Year		China clay (tonnes)	Gypsum (tonnes)	Kyanite (tonnes)	Lime stone (000 tonnes)	Magnesite (tonnes)	Mica (crude) (tonnes)	Salt (000 tonnes)	Steatite (tonnes)	Petroleum (crude) (tonnes)
1960		30 242	83 120	1 680	1 061	13 028	2 436	286	7 783	37 796
1961		30 941	72 132	2 263	1 196	17 479	2 362	288	8 066	42 808
1962		32 250	93 667	4 135	1 363	18 114	2 352	322	8 661	89 770
1963	July	19 896	104 858	1 933	1 400	24 999	2 172	350	8 474	123 109
	August	14 534	99 210	1 610	1 212	28 839	1 971	160	5 700	160 678
	September	16 361	111 852	2 375	1 241	23 870	1 842	126	6 344	152 840
	October	20 881	100 807	2 077	1 344	16 857	1 646	128	8 671	164 409
	November	32 721	87 318	1 598	1 353	15 716	1 644	156	10 042	138 398
	December	39 348	97 595	2 147	1 445	17 259	1 984	116	10 350	199 410
1964	January	44 290	102 928	2 118	1 488	15 142	1 804	133	10 322	158 191
	February	38 884	102 407	2 664	1 385	15 131	1 778	332	11 186	159 806
	March	47 747	105 136	3 069	1 460	14 992	1 802	574	13 654	191 018
	April	48 198	85 703	2 969	1 458	14 882	1 944	8 305	15 273	168 587
	May	47 151	77 280	3 375	1 432	13 496	1 877	1 006	13 153	177 755
	June	26 180	79 680	2 558	1 376	20 051	1 760	1 051	11 457	169 242
	July	...	...	...	...	...	...	173	...	200 393

Monthly Abstract of Statistics, Vol. 17, No. 10, October, 1964.



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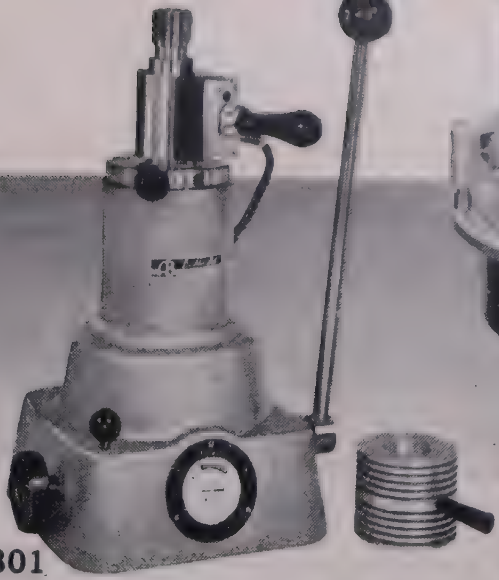

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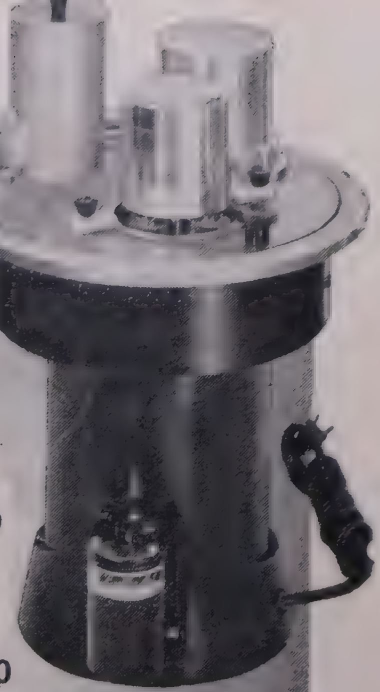

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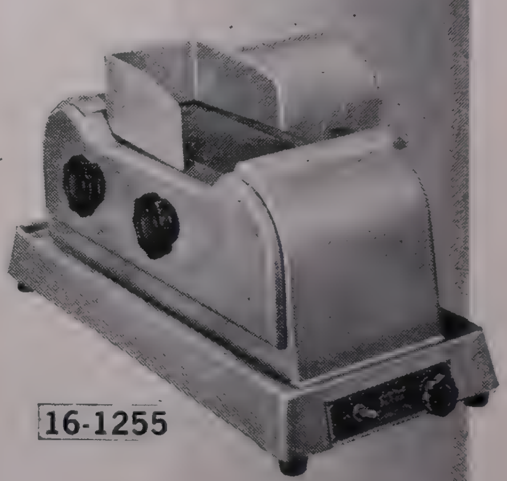

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NML TECHNICAL JOURNAL

VOL. VII No. I FEBRUARY 1965

Symposium on Micro-Metallurgy

MICRO-METALLURGY relating to the role of minute additions to metals and alloys presents a fascinating metallurgical spectrum ranging from basic and fundamental research studies to applied research themes covering the development of alloys and super alloys dependant chiefly for their metallurgical characteristics and physical properties on minute additions of certain elements. The subject of micro-metallurgy, however, is not new. Illustrations of minute additions exercising major damaging effects whilst others conferring equally beneficial properties in the vast and almost unlimited series of ferrous and non-ferrous alloys are abundant—yet the mechanism of how so much is conferred by the so small and the recurring explanations, hypotheses, theories, etc. thereof present to the theoretical scientists and practical metallurgists scope for ceaseless research activity and development applied work. The vast technical literature on the subject, though rich in its technical wealth, presents a wide array of loosely dispersed and scattered technical references in manuals, text books and scientific and technical journals. At the National Metallurgical Laboratory research and development themes to study the role of minute additions to ferrous and non-ferrous metals for the production of diverse ranges of alloys to exacting specifications and needs represent a major field of the laboratory's research activities. The technical and research contributions to this Symposium received from many countries will it is hoped, prove of significant value to the participating Delegates.

It is our privilege and pleasure to welcome the distinguished Delegates from home and overseas to the National Metallurgical Laboratory and a happy landing in our midst. To the warmth of the warming Indian weather, we wish to add the warmth of our welcome.

SYMPOSIUM ON MICRO-METALLURGY—THE ROLE OF MINUTE ADDITIONS TO FERROUS AND NON-FERROUS METALS AND ALLOYS

PROGRAMME

INAUGURAL SESSION

Monday, March 29, 1965

9.00 a.m. to 10.30 a.m.		Registration of Delegates at the NML Main Building
10.30 a.m. to 1.15 p.m.		Visit round the National Metallurgical Laboratory and the Pilot Plants

Break for Lunch

3.30 p.m.	GREETINGS	Dr B. R. NIJHAWAN, *Director,* *National Metallurgical Laboratory,* *Jamshedpur.*
3.35 p.m.	OPENING ADDRESS	Sir JEHANGIR GHANDY, Kt. C.I.E., *Chairman,* *Executive Council,* *National Metallurgical Laboratory,* *Jamshedpur.*
3.45 p.m.	INAUGURAL ADDRESS	Shri ASOKA MEHTA, *Deputy Chairman,* *Planning Commission,* *Government of India, New Delhi.*
3.55 p.m.	ADDRESS	Dr S. HUSAIN ZAHEER, *Director-General,* *Scientific and Industrial Research, New Delhi.*
4.05 p.m.	ADDRESS	Shri M. S. RAO, I.C.S., *Chairman,* *Hindustan Steel Ltd.,* *Ranchi.*
4.15 p.m.	GROUP PHOTOGRAPH	In front of the Main Building of the National Metallurgical Laboratory.
4.25 p.m.	Opening of the New Foundry Block of the National Metallurgical Laboratory	Shri ASOKA MEHTA, *Deputy Chairman,* *Planning Commission, Government of India,* *New Delhi.*
4.45 p.m.	Tea at the Lawn of the National Metallurgical Laboratory	

SPECIAL LECTURES

Monday, March 29, 1965

5.00 p.m.—5.45 p.m.

Chairman	Shri ASOKA MEHTA, *Deputy Chairman,* *Planning Commission,* *Government of India, New Delhi.*
Recorder	Dr T. BANERJEE, *National Metallurgical Laboratory,* *Jamshedpur.*

1. **Micro-Production in the Steel Industry**	Mr J. R. MILLER, *Special Technical Adviser,* *Centre for Industrial Development,* *United Nations* *New York, U.S.A.*
2. **Bismuth in Malleable Cast Iron**	Dr ROBERT H. ABORN, *Consultant to American Smelting and Refining Co., U.S.A.* (To be presented by Mr C. Sharma, National Metallurgical Laboratory)

6.45 p.m. Dances of India—at the NML Auditorium, organised by the NML Club (by invitation)

TECHNICAL SESSIONS

Tuesday, March 30, 1965

Session I

9.30 a.m. to 1.00 p.m.

Chairman	Mr J. R. MILLER, *Senior Technical Adviser,* *Centre for Industrial Development, United Nations.* *New York, U.S.A.*
Recorder	Dr A. B. CHATTERJEA, *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

Titles	*Authors*
1. **Pearlite free structural steels**	J. A. CHAPMAN, R. PHILLIPS, Colvilles Ltd., and Dr R. L. CRAIK, *Head of Laboratories, BISRA, England.*
2. **Rare earth metals in stainless steel making.**	L. NEMETHY, *Manager,* *Atlas India Project, Atlas Steels Company, Ontario, Canada.*
3. **Techniques for the study of micro-phases and their influence on material properties.**	D. SCOTT and A. I. SMITH, DSIR, *National Engineering Laboratory, Glasgow, England.*
4. **The purification of iron by selective prepurification and oxidation zone melting; property measurements and Minor impurity contents.**	B. F. OLIVER, F. GAROFALO, S. ARAJS and R. PRIESTNER, *United States Steel Corpn., Monroeville, U.S.A.*
5. **The Role of Residual trace elements in alloy steels.**	Dr J. M. CAPUS, *Research Laboratories, Gillette Industries Ltd., Reading, Berkshire, England.*

Break for lunch.

Tuesday, March 30, 1965

Session II

2.30 p.m. to 5.30 p.m.

Chairman ... ... Mr J. L. HARRISON,
Manager,
Iron and Steel Processes
British Oxygen Co. Ltd.,
London.

Recorder ... ... Dr S. S. BHATNAGAR,
National Metallurgical Laboratory,
Jamshedpur.

PAPERS

	Titles	*Authors*
6.	**On the transformation of austenite to martensite and the tempering process of martensite in iron-nitrogen system.**	Prof. Y. IMAI, M. IZUMIYAMA and M. TSUCHIYA, *Metallurgical Research Institute,* *Tohoku University,* *Japan.*
7.	**Effect of Molybdenum on the grain boundary relaxation of iron.**	Dr T. R. S. GOEL, *Research and Advanced Development,* *Delco Radio Division, Kokomo and* Dr F. H. VITOVEC, *Departments of Minerals and Metals and Nuclear Engineering,* *University of Wisconsin, U.S.A.*
8.	**The effect of a small amount of vanadium and niobium on the micro-structures and the strength of pro-eutectoid ferrite of iron-carbon alloys.**	M. TANINO, T. NISHIDA, T. OOKA and K. YOSHIKAWA, *Tokyo Research Institute,* *Yawata Iron and Steel Co. Ltd.,* *Japan.*
9.	**Effect of minor elements on normal grain growth in singly oriented silicon iron.**	M. IMAI, T. SAITO, K. TSURUOKA and M. NISHIDA, *Technical Research Laboratory,* *Kawasaki Steel Corporation,* *Kobe, Japan.*

5.40 p.m. TEA

Wednesday, 31 March, 196

Session III

9.30 a.m. to 1.00 p.m.

Chairman	Dr R. L. CRAIK, *Head of Laboratories,* *Metallurgy Division,* *BISRA, Sheffield.*
Recorder	Dr RAJENDRA KUMAR, *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

	Titles	*Authors*
10.	**Scope of Research in Micro-Metallurgy at the National Metallurgical Laboratory.**	Dr B. R. NIJHAWAN, *Director,* *National Metallurgical Laboratory,* *Jamshedpur.*
11.	**Micro-Metallurgy of abnormality in steels**	Dr B. R. NIJHAWAN, Dr A. B. CHATTERJEA and Dr S. S. BHATNAGAR *National Metallurgical Laboratory,* *Jamshedpur.*
12.	**Micro-Metallurgy of austenitic grain size control of steels.**	Dr A. B. CHATTERJEA and Dr B. R. NIJHAWAN, *National Metallurgical Laboratory,* *Jamshedpur.*
13.	**Effect of aluminium additions on the primary grain size of steel castings.**	Dr K. B. MEHTA, *Dy. General Manager (Tech.),* *Heavy Engineering Corpn. Ltd.,* *Ranchi.*
14.	**Effect of Micro Impurities and Alloying Elements on Zirconium and Zircaloy-2.**	H. C. KATIYAR, P. PANDE, K. B. MOORTHY and N. K. RAO, *Atomic Energy Establishment,* *Trombay.*
15.	**Distribution and function of micro-phases and micro-additions in metals and alloys.**	Mr L. J. BALASUNDARAM and Dr RAJENDRA KUMAR, *National Metallurgical Laboratory,* *Jamshedpur.*

Break for lunch

Wednesday March, 31 1965

Session IV

2.30 p.m. to 5.00 p.m.

Chairman	...	...	Mr D. SCOTT, *Head of Metallurgy Section,* *Department of Scientific and* *Industrial Research,* *National Engineering Laboratory,* *Glasgow, England.*
Recorder	...	...	Mr B. N. DAS, *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

	Titles	*Authors*
16.	**Morphology and Polygonisation of copper whiskers in the form of ribbons.**	Mrs B. MINARI, Dr H. J. LATIERE and Mr R. MICHAUD, *Centre de Recherches Physiques CNRS,* *France.*
17.	**Importance of Micro-Metallurgy in Non-ferrous metals and alloys used in Navy.**	G. VENKATESWARLU, *Naval Chemical and Metallurgical Laboratory,* *Bombay.*
18.	**Influence of small amounts of Boron and Zirconium on Hot working characteristics and creep rupture properties of some vacuum melted nickel base alloys.**	Lt. Cdr. V. N. MADHAV RAO and Dr R. V. TAMHANKAR, *Defence Metallurgical Research Laboratory,* *Hyderabad.*
19.	**Effect of minor additions of alloying elements on irradiation behaviour and mechanical properties of natural metallic uranium.**	K. BALARAMAMOORTHY, H. C. KATIYAR and N. K. RAO, *Atomic Energy Establishment,* *Trombay.*

5.40 p.m. TEA

Thursday, April 2,

Session V

9.30 a.m. to 1.00 p.m.

Chairman	...	...	Mr J. L. YOUNG, *Management Consultant,* *The Ford Foundation* *New Delhi.*
Recorder	...	...	Mr P. K. GUPTE, *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

	Titles	*Authors*
20.	**Effect of Bismuth Additions on the Graphitization of spheroidal graphite cast iron.**	Dr CARL R. LOPER, *University of Wisconsin,* *Department of Minerals and Metallurgical Engineering, U.S.A.*
21.	**Surface tension of cast iron with additions of different elements.**	JATINDER MOHAN, *National Metallurgical Laboratory,* FRANCIS MOSTOR and Dr Ing. C. PELHAN, *Metalurski Institute, Ljubljana, Yugoslavia.*
22.	**Determination of the distribution of impurities in commercial beryllium by electron microscopy.**	M. CROUTZEILLES and J. MORICEAU, *Metallurgical Research Centre,* *Pechiney, France.*
23.	**Studies on micro constituents in metals and alloys by the electron microprobe and by some specialised chemical technique aided with x-ray diffraction.**	Dr G. P. CHATTERJEE, Dr B. P. SEN and Dr J. BHATTACHARJEE *Hindustan Steel Ltd., Durgapur.*
24.	**Effect of Trace Elements on Ageing of some aluminium-base alloys.**	Dr VED PRAKASH, *National Metallurgical Laboratory,* *Jamshedpur.*
25.	**Study of micro-additions to Al-Mg wrought alloys.**	Dr Y. N. TREHAN, S. P. BHADRA, P. K. GUPTE and Dr B. R. NIJHAWAN, *National Metallurgical Laboratory,* *Jamshedpur.*

Break for lunch.

Thursday, April 1, 1965

Session VI

2.30 p.m. to 5.00 p.m.

Chairman	...	...	Dr B. R. NIJHAWAN, *Director,* *National Metallurgical Laboratory,* *Jamshedpnr.*
Recorder	...	...	Mr R. M. KRISHNAN, *National Metallurgical Laboratory,* *Jamshedpur.*

PAPERS

	Titles	*Authors*
26.	**Some observations on recent methods of analysis of gases in metals and alloys.**	N. G. BANERJEE, *National Metallurgical Laboratory,* *Jamshedpur.*
27.	**A spectroscopic method of determination of micro-amounts of elements in steels.**	R. D. NAIDU and Miss M. NIRMALA, *Defence Metallurgical Research Laboratory,* *Hyderabad.*
28.	**Spectrographic analysis of micro-elements in Metals and Alloys.**	M. K. GHOSH, P. C. DEBNATH, Miss SUMITRA DASGUPTA, and Dr B. C. KAR, *National Metallurgical Laboratory,* *Jamshedpur.*
29.	**Analytical methods in micro-metallurgy.**	P. KOTESWARA RAO, S. L. N. ACHARYULU and M. K. JOSHI, *Defence Metallurgical Research Laboratory,* *Hyderabad.*
	CLOSING REMARKS	Dr B. R. NIJHAWAN, *Director,* *National Metallurgical Laboratory,* *Jamshedpur.*

5.10 p.m. TEA

Abstracts of papers—Symposium on Micro-Metallurgy—The Role of Minute Additions to Ferrous and Non-ferrous Metals and Alloys

1

Pearlite free structural steels

J. A. CHAPMAN, *BISRA*, R. PHILLIPS, Colvilles Ltd., and Dr R. L. CRAIK,
Head of Laboratories, BISRA, England.

2

Rare earth metals in stainless steel making

L. NEMETHY,
Manager, Atlas India Project, Atlas Steels Company, Ontario, Canada.

THE effects of grain refinement and precipitation hardening conferred by minor additions of Nb and V have been studied in both as rolled and normalised low carbon experimental steels. The mechanical properties of such steels are outlined and related to their structures.

A considerable amount of research has been done between 1950 and 1960 in the US and Canada using various types of Rare Earths to improve certain properties of Cr-Ni austenitic stainless steels. After encouraging research work, almost all Stainless Steel Producers started field application of Rare Earths primarily to improve yield by eliminating poor 'Hot Workability' of certain chemically 'unbalanced' alloys. Only a very few papers were published in those years basically because of contradicting results. Several patents have been granted in the U.S. and the Special Alloy Manufacturers anticipated a very bright future for the future use of these elements. Rare Earths are plentiful and chemists were working with them during the past 150 years. Their separation was expensive and scarce. With the wide use of Thorium in nuclear technology, large quantities of Rare Earths became available as a by-product after World War II.

Despite the relative abundancy, the use of Rare Earths is more and more limited in the Steel Industry and was practically withdrawn by 1960 from the manufacture of stainless steels in North America. Suprisingly, authors from other countries claimed recently that the addition of Rare Earths to stainless steels can improve 'Hot Workability' and permit the reduction of Ni content from 10·6% to 9·6% resulting in significant cost saving.

It appears proper to review the history of making stainless steels with the addition of Rare Earths, particularly in light of recent work on properties of Rare Earths.

It is unfortunate that most of the scientific work on phase diagrams, thermodynamic properties of Rare Earth alloys were not known at the time the Stainless Steel Industry experimented with their use, as most of the work of this nature was published after 1960. The information avilable to-day is still far from being complete but it is certainly confirmative for the discontinued use of Rare Earths for stainless steels.

The present paper will discuss: (i) The Chemistry of Rare Earths (ii) Historical Review of Experimental work in Connection with Stainless Steels (iii) Physical Properties of Rare Earth metals (iv) Alloying Behaviour of Rare Earth metals (v) Rare Earths—Stainless Steel experiments done by ATLAS (vi) Interpretation of Results in light of thermodynamical data available.

It can be concluded that further specific work is needed to investigate some properties, the improvement of which could justify the expensive use of Rare Earths additions.

3

Techniques for the study of micro-phases and their influence on material properties

D. SCOTT and A. I. SMITH, DSIR,
National Engineering Laboratory, Glasgow, England.

IN modern materials research the necessity of studying processes in great detail requires the application of special techniques. Several advanced techniques are available for the study of micro-phases and their influence on material properties. Specific information from each technique enables comprehensive data to be obtained. Various techniques and equipment are briefly described.

Electron microscopy is used for the study of fine-scale structural details and electron microfractography for the investigation of failure initiation, mode of failure and the influence of minor constituents. Elegant extraction replica techniques are available for the study of precipitates and electron and X-ray diffraction is used for their identification. Thin foil techniques provide a quantitative approach and a three dimension structural picture. The use of heating, straining and cooling stages in the electron microscope allows events to be followed as they occur and to be recorded by sequential and cine-photography.

Electron probe X-ray microanalysis is used for the study of solution segregation problems, diffusion couples, composition of oxide films, non-metallic inclusions, precipitates, precipitate and nucleation processes, grain boundary and denudation effects, etc.

Potentially powerful new techniques such as the application of probe analysis to the light elements and ion-beam micro-analysis for the identification of isotopes are being developed. New developments such as emission electron microscopy for observing solid surfaces and extending the range of hot-stage microscopy to the electron optical range and the study of temperature-dependent changes as they occur are being assessed.

The potential advantage of the development of new equipment such as the combination of scanning, transmission electron microscopy and probe analysis in one instrument is discussed.

The paper reviews, with a comprehensive list of references to published work, the techniques for study of fine-scale physical processes in metals. The advantages of several techniques are discussed and illustrated by relevant work NEL. This includes studies of the effect of N in Al and Si killed steels, negative creep, structural changes in creep, vacuum melting reduction of impurities in ball bearing materials, tin oxide problem in bearings and H embrittlement, etc.

4

The purification of iron by selective prepurification and oxidation zone melting ; property measurements and Minor impurity contents

B. F. OLIVER, F. GAROFALO, S. ARAJS and
R. PRIESTNER,
United States Steel Corpn., Monroeville, U.S.A.

GAS-metal oxidation reactions and zone-melting (OZM) were simultaneously employed to produce several high-purity irons in a levitating zone melter. Vacuum melted commercial electrolytic iron and iron produced from hydrogen reduction of distilled ferric chloride were given the OZM treatments. Initial and final analyses for substitutional elements were obtained by mass spectrometric methods.

Irons ranging in purity from 99·89 to approximately 99·998 + with low interstitial contents have been prepared. The major uncertainty in the purity is related to the inability to reliably analyze for oxygen below 20 ppm.

No measureable gradient in the residual carbon content was observed along the entire zone-melted length (6-10 inches) in one-inch diameter bars. The absence of a carbon concentration gradient in the solid indicates an apparent distribution coefficient of 1, an unusual condition.

state extraction analyses indicate that the mobile carbon in α-iron depends on the gas-metal heterogeneous reactions employed. Purification under an oxidizing atmosphere resulted in the immobilization of nearly all of the carbon present at levels of 10 ppm or less. Continuation of purification in a reducing atmosphere returned the carbon to a state of mobility which was again reversed by further purification in an oxidizing atmosphere. The immobilization of carbon at 'residual levels' is believed to be associated with a strong interaction between carbon and oxygen atoms.

Irons with low carbon and nitrogen contents which did not exhibit a hot-hardeness peak were produced after subsequent zone-melting in vacuum.

Tensile stress strain measurements at temperatures below 300°K revealed yield point phenomena both in those irons which did and in those which did not exhibit carbon mobility in hot hardness tests. Although the nature of the upper yield differed among the two categories, in both of them the upper and lower yield points were highly temperature sensitive in the temperature range where deformation twinning was absent. Return of the yield point by low temperature ageing was, in the one case, attributed to carbon diffusion, and in the other case to the diffusion of lattice defects created during prior straining.

Thermal conductivity (λ) of a high-purity iron (99·998+%Fe) has been studied as a function of temperature (T) between 7 and 200°K. Equivalent data is presented for an iron of 99·8% purity. The λ vs T curve for the iron of higher purity reaches a maximum of about 15 W cm^{-1} $°K^{-1}$ at 21°K. This value is considerably larger than that of 4·5 W Cm^{-1} $°K^{-1}$ previously observed by Kemp et al in 1959. Our measurements are in qualitative agreement with the theoretical expectations for a high-purity iron. The problem, associated with accurate determination of the Lorenz number and the thermal resistivity due to electronphonon scattering at low temperatures in iron, is briefly discussed.

5

The Role of Residual trace elements in alloy steels

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RECENT work in the U.K. on the influence of residual trace elements on the mechanical properties of constructional alloy steel is reviewed. The most fruitful approach has been through the 'synthesis' of high-purity steels. This has enabled the effects of individual trace elements to be studied by making separate small additions.

Thus temper-brittleness can be caused by minute traces of phosphorus, arsenic, antimony or tin, or by much larger amounts of silicon or manganese. The embrittlement of quenched and tempered alloy steels around 350°C can be promoted also by nitrogen.

On the other hand, in high-temperature embrittlement and cast brittleness, as well as the brittleness encountered in welding, sulphur is a contributing element. These phenomena are not well understood.

The deleterious effect of minor residual elements limits the development of alloy steels, particularly for high stength applications, and efforts are now being directed towards purer as well as cleaner steels.

6

On the transformation of austenite to martensite and the tempering process of martensite in iron-nitrogen system

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THE transformation of austenite to martensite and the tempering of martensite in iron-carbon system, have been investigated by several workers but very few studies have related to the problem in iron-nitrogen system, in spite of the fact that both nitrogen and carbon have similar atomic volumes and that a forced interstitial solid solution is formed in iron.

In the present work the authors have studied the transformation of austenite to martensite based on statistical thermodynamics and crystallography using Fe-N alloys, and have compared the results to those obtained with Fe-C alloys. Studies on tempering of martensite and austenite in Fe-N alloys were carried out by X-ray diffraction analysis.

7

Effect of Molybdenum on the grain boundary relaxation of iron

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GRAIN boundary segregation of molybdenum in iron at a range of composition from 0·0006 a/o (0·001 w/o) molybdenum (zone refined iron) to 0·24 a/o (0·41 w/o) molybdenum was studied by internal friction techniques and X-ray microradiography. The activation energy for grain boundary segregation of molybdenum in iron was calculated to be 5 300 cal/mole. This information was used to select the appropriate heat-treating conditions which would promote grain boundary segregation. The segregation of molybdenum in the test samples was verified by X-ray microscopy using Co-$K\alpha$ radiation.

The internal friction spectrum was determined from flexural resonant vibrations of cylindrical specimens during cooling in a protective atmosphere. Magnetic damping effects were suppressed during the internal friction measurements.

The internal friction peaks observed fall in the same general temperature range as the grain boundary relaxation peaks of iron which are reported in the literature. The activation energy for grain boundary relaxation increases from 54 400 cal/mole for zone refined iron rapidly at first with increasing molybdenum addition and levels off at higher concentrations. This variation indicates that grain boundary saturation by molybdenum is reached at approximately 0·065 a/o (0·11 w/o) Mo.

The temperature of the internal friction peaks increases somewhat whereas the magnitude of the internal friction peak values decreases rapidly with increasing molybdenum concentrations. A new peak could be attributed to molybdenum was not observed within the range of compositions investigated.

The data agree with the concepts of Mott's island model of the grain-boundary structure in general. The solute atoms when adsorbed at the grain bounaries improve the fit at the boundaries and reduce the lattice and grain boundary strain energies. The velocity of sliding decreases, while the grain boundary viscosity, the number of atoms surrounding an 'area of good fit' and the rate constant increase with increasing bulk, concentration of molybdenum in iron.

8

The effect of a small amount of vanadium and niobium on the micro-structures and the strength of pro-eutectoid ferrite of iron-carbon alloys

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AN investigation was carried out to elucidate the strengthening effect of vanadium and niobium added to the 0·2% carbon steels by means of the transmission electron microscope.

It was found that the strength of proeutectoid ferrite in steels containing vanadium and niobium was generally higher than that in plain carbon steels, and that the maximum strength could be obtained when cooled approximately at 60–80°C/min.

ectoid ferrite by addition of vanadium and niobium was attributable to the formation of substructures containing various types of lattice defects and extremely fine particles of vanadium and niobium carbide. In the substructures we have (1) dislocation loops and carbide particles uniformly distributed in ferrite matrix, (2) dislocation dipoles, (3) rows of carbide particles and (4) micro-twins which seem to be a kind of transformotion twin.

The mechanism of formation of such substructures is discussed. The fact that a considerable number of micro-twins were found suggests that the stacking fault energy of alpha iron is considerably lowered by addition of vanadium.

The crystallographic orientation relationship between vanadium carbide and ferrite matrix has been determined.

The result is as follows ;

$$(100)V_4C_3//(100)\alpha-Fe, \ (010)V_4C_3//(011)\alpha-Fe, \ (001)V_4C_3 \ (011)\alpha-Fe$$

9

Effect of minor elements on normal grain growth in singly oriented silicon iron

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THE normal grain growth behaviour of cold rolled 3% Si—Fe sheet was investigated. The rate of primary grain boundary migration was strongly retarded by the existence of minute quantities of impurity elements such as Ag, Au, Cu, Ni, Ti, Nb, Sb, S, Se, and Te. The free energy of activation for primary grain boundary migration ($\triangle F_A$) was calculated. In specimens containing sufficient addition amount of these elements, $\triangle F_A$ takes a value in close agreement with the free energy of activation for lattice self-diffusion of alpha iron. Impurity atoms with a low intragranular solubility will segregate preferentially at grain boundary because they can there reduce the misfit energy, and then the free energy of activation for boundary migration will tend towards a value approaching that characteristic of lattice self-diffusion.

10

Scope of Research in Micro-Metallurgy at the National Metallurgical Laboratory

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Director, National Metallurgical Laboratory, Jamshedpur.

THE scope of research in ‘micro-metallurgy’ bridges across the work of fundamental research studies and that of applied development themes thereby providing the link between theory and practice. The subject of ‘micro-metallurgy’, however, is not new-almost a decade back, at one of the N.M.L. Symposia, the role of ‘micro-metallurgy’ in relation to alloy steels was discussed with particular reference to some pioneering work undertaken on the subject at the National Metallurgical Laboratory. Basic and applied researches on diverse facets of ‘micro-metallurgy’ have since been pursued at the National Metallurgical Laboratory; some of the themes have related to effects of micro-additions on grain-size control of steel and on abnormality, strain-ageing effects in steel in relation to residual micro-constituents, micro-additions of rare earths to stainless steels and aluminium-magnesium alloys, micro-metallurgy of liquid metals, ageing of aluminium alloys in relation to trace elements, studies on phase changes in relation to micro-constituents, micro-metallurgy of aluminium-silicon alloys and heat resistant alloys and analytical techniques for measuring micro-additions to alloys. In this paper, a review has been made of some of the highlights of research results obtained in the foregoing broad themes whilst indicating current thinking on the subject and outlining fresh fields for future work along the line. The subject of 'micro-metallurgy' is of-course, vast indeed and as such, requires priorities to be assigned, cataloguing of observed hypotheses and defining those needing focussed attention, particularly in relation to research facilites and equipment avilable for introducing specialized research techniques. Research studies undertaken so far have been fully rewarding whilst the search and research on, how so much is conferred by the so minute, present a fascinating metallurgical spectrum for unending research programming, in the planing and execution of which, the National Metallurgical Laboratory currently is actively engaged upon.

11

Micro-Metallurgy of abnormality in steels

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THE subject of 'abnormality' in steels has of late, somewhat receded in the background, even though its practical importance has not diminished. Factors influencing abnormality are related to the micro-presence of aluminium, oxygen, nitrogen, etc. in hyper-eutectic zones of carburized steels; each of these factors has been well investigated and reported upon this paper. The degree of abnormality in different depths of the case-carburized zone of the steel was observed to be affected by the formation of Al_2O_3 as also possibly of AlN in the relevant zones. Carburization treatments with and without oxygen and nitrogen were carried out to substantiate some of the observations made. Steels containing micro-contents of aluminium optimum for austenitic grain growth inhibition, were likewise investigated. The subject of 'abnormality' in steel which perhaps owed its origin to case-carburization treatments to promote high surface hardness and came to limelight following the presence of 'abnormal soft spots', is none-the-less important and interesting from both theoretical and practical stand points, despite the development of alternative modes of surface-hardening other than case-carburization.

12

Micro-Metallurgy of austenitic grain size control of steels.

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MICRO-ADDITIONS of aluminium and nitrogen to steels exercise significant effects on their austenitic grain growth characteristics and physical properties. Effects of such micro-additions judiciously made, in relation to the properties, isothermal transformation characteristics, MS points and grain-growth characteristics of steels have been outlined in this paper. Grain refinement enhanced the impact toughness without affecting the tensile strength of some plain carbon steels. In nickel-chrome steels, grain refinement reduced the susceptibility to temperbrittleness. The phenomenon of abnormal grain growth was comprehensively investigated and earlier hypotheses based on the role therein of sub-microscopic Al_2O_3 particles, residual aluminium and aluminium sulphide were found untenable. Intergranular precipitation was observed on soaking the steels in nitrogen and the precipitated phase was identified as aluminium nitride. The aluminium nitride contents of the steels decreased with rise in temperature. The solution temperature of aluminium nitride in austenite fairly agreed with the grain-coarsening temperature of the steels. In steels containing optimum micro-addition of aluminium, isothermal grain growth below the grain coarsening temperature was not conspicuous. The size, distribution and agglomeration of AlN at higher temperatures were significantly affected by the residual aluminium contents of the steel. It was established that in

cipitation of AlN provided the requisite grain growth inhibition whilst its solution led to abnormal grain growth. The agglomeration of AlN in high aluminium bearing steels caused the reversion to normal grain growth behaviour. Some results of electron-diffraction studies of steels containing micro-contents of aluminium following nitrogen treatment, established the sub-microscopic precipitated phase to be AlN-an observation which finds scanty reference in the technical literature on the subject.

13

Effect of aluminium additions on the primary grain size of steel castings

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THEORIES of grain-refinement of castings have been put forward on the basis of liquid-solid nucleation by the process of 'Kindred' and 'Foreign' nuclei and crystal growth in the melt. A theory has been developed on the basis of foreign nuclei due to small additions of titanium and other metals in the case of aluminium alloy sand castings. This accounts satisfactorily for the way in which grain refinement takes place and appears to be of more general application. The present investigation is initiated to find out the extent to which this theory can be applied to the refinement of the macrostructure and inherent as—solidified grain size of steel during casting operations by the addition of aluminium and, in particular, whether there is a close relationship between the lattice of nucleating particles and that of the solidifying metal. Attempts have also been made to study the casting conditions snch as the state of deoxidation of the melt, casting temperature, pouring rates and turbulence of the melt during solidification and to relate these to the as-cast primary structure in steel castings.

14

Effect of Micro Impurities and Alloying Elements on Zirconium and Zircaloy-2

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RESISTANCE to corrosion in high temperature water and to radiation damage and retention of strength to moderately high temperatures are some of the important factors that have promoted zirconium and its alloys as canning and structural materials for atomic reactor cores.

These properties are very much affected by impurities like oxygen, hydrogen and nitrogen etc. An attempt has been made to review the effect of these impurity levels in zirconium and zircaloy-2. The effects of other alloying elements are also described.

15

Distribution and function of micro-phases and micro-additions in metals and alloys

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THE paper begins with an introduction to the fundamental thermodynamic factors responsible for the hunger of metals for solutes. In addition to the discussion of micro-additions, the influence of micro-phases and imperfections is also discussed.

The distribution of micro-constituents is discussed in the liquid and solid states. It is shown that in liquids, solute atoms are usually present in the form of clusters. The influence of the clusters and other heterogenities on solidification and subsequent mechanical properties is then brought out.

In the solid state, micro-constituents in metals and alloys exert their influence either by themselves when present in solution in the matrix, or as micro-phases. After discussing the distribution of micro-constituents on imperfections and grain boundaries, their influence on crystal structure, plasticity, electrical and mechanical properties, phase transformations (including pre-precipitation phenomena, internal oxidation and internal

boundary movements) and morphology of phase distribution is discussed in this paper.

An attempt has also been made to correlate the micro-additions (and substractions) with the mechanical properties.

16

Morphology and Polygonisation of copper whiskers in the form of ribbons

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IT was shown that the fundamental element of whiskers in the form of ribbons is the plate. This mainly consists of a network of ramifications. In this paper the authors have studied the structure of the link separating two plates and have given an example of ribbon-shaped 'whiskers' on the surface of which, the attack patterns produce the boundaries between sub-grains. These are brought in evidence by X-ray diffraction. From these morphological aspects it is deduced that the ribbon-shaped whiskers are rich in dislocations. Besides, it was found that an anneal under elastic constraint leads to polygonisation and it is concluded that this could not be explained unless the presence of dislocations is assumed in the initial ribbon. Finally, polygonisation does not affect the exceptional elastic properties of these whiskers. From a practical point of view, such behaviour could be of very important consequences.

17

Importance of Micro-Metallurgy in Non-ferrous metals and alloys used in Navy

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VAST quantities of copper and copper alloys are used in ship's machinery such as condenser, drain cooler, oil and water cooler. In presence of seawater, these alloys suffer dezincification and impingement attack. Resistance to dezincification and impingement attack has been imparted to the alloys by minute addition of alloying elements. The paper describes some of these important non-ferrous alloys used in the Navy where minute addition of alloying elements have improved their properties.

A small addition of arsenic (0·02 to 0·06 per cent) inhibits the dezincification in alpha brasses used for condenser tubes. Addition of small amounts of antimony or phosphorus have a similar effect on these alloys. Addition of 0·03 to 0·45%. iron improves the resistance to impingement attack of cupro-nickel alloys in seawater environment. Aluminium bronzes containing small amounts of silicon, nickel or iron have high strength and corrosion resistance. The role played by the minor alloying elements are discussed in the paper.

18

Influence of small amounts of Boron and Zirconium on hot working characteristics and creep rupture properties of some Vacuum melted nickel base alloys

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NICKEL base precipitation hardening alloys which are extensively used for high temperature services particularly in Gas Turbine Engines are prone to heat variation in properties even though their nominal chemical composition is constant. Boron and Zirconium present in trace amounts in some nickel base alloys, have been noted to have significant influence on their hot working characteristics and creep rupture properties.

Details of experimental work directed towards solving the perplexing problem of melt to melt variations of some of these alloys and the conclusions drawn thereof with respect to influence of Boron and Zirconium have been discussed.

Conditions attending on Vacuum melting practice with reference to contamination of the melt by these two elements as a result of melt refractory crucible reaction have been dealt with. Results of investigations carried out to evaluate influence of Boron and Zirconium teristics and creep rupture properties of these alloys have also been discussed. The advantageous effects derived by allowing within controlled limits, these two elements individually and also simultaneously on such properties as well as the effects of their mutual interreaction on the hot working characteristics, in particular. of these alloys have been covered.

Particular attention has been drawn to the specific advantages of adopting vacuum melting in the case of such alloys, whereby the scatter in the properties from melt to melt due to uncontrolled trace amounts of Boron and Zirconium could be eliminated. The marked improvements in rupture life and ductility obtained by controlled additions of these elements have been discussed.

19

Effect of minor additions of alloying elements on irradiation behaviour and mechanical properties of natural metallic uranium

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THE basic nuclear fuel for reactors is uranium. Natural Pollycrystalline untreated uranium metal is mostly unstable during irradiation restricting its use for higher burn-ups, which led to the develoment of alloying it with other elements.

The behaviour of unalloyed uranium under irradiation and under thermal cycling test has been described. The effect of minor additions af alloying elements to uranium has been reviewed. The achievement of good stability and improved mechanical properties of U-Mo and U-Al alloys has been emphasised.

20

Effect of Bismuth Additions on the Graphitization of spheroidal graphite cast iron

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LITERATURE on the effect of bismuth on the structure and properties of ductile iron, gray cast iron, and malleable iron is reviewed. The significance of the ductile iron processing cycle in graphitization is emphasized as is the necessity to study ductile iron in close association with processing techniques. Test castings of hypereutectic, ductile irons were produced with and without the addition of metallic bismuth up to 0·015 percent. Test castings were examined for primary and secondary carbide formation and graphite spheroid size, shape, and distribution. Bismuth additions in ductile iron were shown to increase nodule counts, reduce the presence of vermicular graphite, and effect a reduction in primary carbide. The role of bismuth in controlling graphitization during solidification is described and the fact that bismuth is a subversive element is refuted. The role of bismuth in ductile iron is further dicussed in relation to the processing cycle.

21

Surface tension of cast iron with additions of different elements

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SURFACE tension is a fundamental thermodynamic property of a liquid surface and serves as an accurate index of the relative magnitudes of other properties of the liquid state. Surface tension which has its origin in intermolecular attraction, constitutes an important source of data for evaluating certain important properties of the transition region between the liquid and solid phase, surface energy and interfacial energies.

In the present study, surface tension of the Swedish iron with and without 0·05 and 0·5 percentage additions of some elements was studied by capillary-rise method. It was observed that 0·05 percentage addition of Si, Mo, P, Ca, Va, Ni and Cr caused rise in surface tension than that of base Swedish iron ; whereas with the same percentge addition of Al, Ti, Pb, Mn, S and Zn to the

Swedish iron, the surface tension was lowered; Sb, Sn and Cu however, did not show any important effect thereon. On increasing the percentage from 0·05 to 0·5 of Ti, Mn, Zn and Cu to the base iron, the latter showed higher surface tension. Vanadium which caused somewhat higher surface tension upto 0.05% addition, did not affect the surface addition when added singly upto 0·5%. With the increase from 0·05% to 0·5% of Sb, Sn, S, Al to the base iron, the surface tension was further lowered.

22

Determination of the distribution of impurities in commercial beryllium by electron microscopy

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ELECTRON microscopy and microdiffraction techniques were applied to the study of the distribution of impurities in the alloys Be-Fe, Be-Al and Be-Si, and in several varieties of commercial beryllium.

Heat-treatments have no influence on some of the impurities which always remain out of solution either as aluminium or silicon, or as the intermetallic compounds $Be_{13}M$ or $Be_{12}X$.

Iron plays an importont part. At 800°C (1472°F), beryllium can dissolve 0·25% iron. Ageing treatments between 500°C (932°F) and 700°C (1292°F) precipitate the oriented phase $Be_{11}Fe$, mainly in the grain boundaries.

In presence of aluminium, the solubility of iron in beryllium is greatly decreased. The natures of the precipitate appearing during ageing treatments at 500°C and 700°C depend upon the temperature of the solution heat-treatment: when the metal is quenched from 950°C (1742°F), only Be_5 (Fe, Al) precipitates, but a solution treatment at 1100°C (2012°F) induces the precipitation of a mixture of Be_5 (Fe, Al) and Be_{11}-Fe. This phenomenon occurs even when the iron and aluminium contents are very small (35 ppm).

The precipitates appear in the boundaries and decorate the dislocations within the grains.

23

Studies on micro constituents in metals and alloys by the electron microprobe and by some specialised chemical technique aided with x-ray diffraction

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DIFFERENT micro-constituents in a metallic specimen can be studied with optical micrcscope and by X-ray or electron diffraction and microscopy. All these techniques provide specific informations with regard to the different phases and micro-constituents present in metals and alloys. In recent years another powerful technique namely the technique ef Electron Microprobe analysis has been successfully utilised in getting informations about the micro-constituents in metals and alloys as well as non-metallic materials.

An attempt has been made in this paper to study the nature of different micro-constituents in metals and alloys with particular reference to steel. The so-called ferrite banding in steel is often attributed to micro segregation of phosphorus. With the help of the Electron Microprobe it was proved that banding may occur for reasons other than phosphorus segregation. The informations obtained from Electron Microprobe studies have been of considerable help to devise ways and means to eliminate the so-called banding in the micro-structructure of steel. By specialised chemical technique it has been possible to study the nature of some of the inclusions in steel.

24

Effect of Trace Elements on Ageing of some aluminium-base alloys

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AGEING of an alloy an element, which may result in retardation of natural ageing effects or acceleration of induced ageing. Lowering of ageing capacity in an alloy is purely related to phase changes that the minute additions of an element can bring about. Such changes may result in marked depletion of the alloying element mainly responsible for ageing. Other two effects may be purely physical in nature and are discussed in this paper in some details. Hardy and others had observed that when elements, such as tin, bismuth, lead, magnesium, cadmium or silver are present in quantites~0·1% in Al-4% copper alloys, the former can almost wholly suppress the natural ageing of the latter and accelerate the induced ageing effects by a factor of 3 to 8; such effects have been discussed in this paper in terms of (a) interaction of these elements with vacancies, and (b) creation of additional nucleation sites for pre-cipitation.

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Study of Micro-additions to Al-Mg wrought alloys

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THE solubility of magnesium in aluminium decreases from 15·3 per cent at 450°C to 3 per cent at 200°C and further to about 1 per cent at room temperature, which should render the aluminium-magnesium alloys susceptible to precipitation-age-hardening particularly in the range of 7–10% magnesium; in practice, however, the latter alloys reveal abnormally low response to precipitation-age-hardening. Increased hardening response may, however, be induced by small additions of zinc, silver and copper. This paper outlines some of the research results obtained at the National Metallurgical Laboratory on the effects of additions of misch-metal upto 3%, silver upto 0·1% and copper upto 0·1% to Al-7% Mg alloys in relation to their response to precipitation-age-hardening. It has been observed that the additions of misch-metal do not cause any significant change in the hardness of the alloys after ageing. Additions of silver and copper improve the response to age-hardening at 250°C of Al-7% Mg alloys; Such improvement is perceptible on ageing for 24-100 hours after quenching from the solution-treatment temperature. After a peak hardness is reached, the latter drops ultimately attaining the hardness value almost equal to that of the solution-treated alloy. Changes in the tensile strength and 0·1% proof stress have also been studied in the alloys treated under similar conditions, or kept for long periods at room temperature. An increase in the 0·1% proof stress has been observed on ageing. These results have been discussed in relation to some of the theoritical implications of micro-additions to Al-Mg wrought alloys.

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Some observations on recent methods of analysis of gases in metals and alloys

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VACUUM fusion gas analysis has long been used as a standard method for the determination of oxygen, nitrogen and hydrogen in metals and alloys. Conventional methods in use for determination of nitrogen and hydrogen, their merits and demerits are discussed in this paper. Some modifications in vacuum fusion analytical techniques recently introduced have also been outlined. One modification involves the use of emission spectrography to estimate oxygen, nitrogen and hydrogen in metals by melting the sample and extracting the gaseous elements with a d.c. carbon arc discharge in pure argon. Attempts have been made recently to use radio-activation, isotopic dilution and isotopic balancing methods for estimation purposes. Determination of oxygen in beryllium has successfully been achieved by activation with a wide variety of bombarding particles. The method of isotopic dilution has been developed for the determination of oxygen and nitrogen in copper, titanium, zirconium, steel etc. The method of isotopic balancing has been developed for the determination of hydrogen only. The paper also gives the description of the vacuum fusion gas analysis apparatus and hot extraction hydrogen determination apparatus fabricated at the National Metallurgical Laboratory. Some information on the new method for the determination of nitrogen in solid solution by electro-chemical method has also been furnished.

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A spectroscopic method of determination of micro-amounts of elements in steels

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THE paper describes a method of spectrographic determination of small amounts of elements of importance in metals and alloys which sometimes exert a great influence on the metallurgical properties. Such elements in metals and alloys may either be residues with deleterious or beneficial effects or additions made to obtain special properties in the alloys.

A brief survey of the influence of small amounts of elements in certain alloys of importance to defence has been made and a method of Spectrographic determination of these trace amounts of some elements in steel has been described. The co-efficient of variation to assess the precision of the method is given.

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Spectrographic analysis of micro-elements in Metals and Alloys

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Miss SUMITRA DASGUPTA
nad Dr B. C. KAR,
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MINUTE additions of certain elements to both ferrous and non-ferrous metals and alloys exercise pronounced effects on their metallurgical characteristics and physical properties. To study such effects, accurate analyses of the minute additions are required. Methods for the spectrographic analysis of micro-constituents in ferrous and non-ferrous metals and alloys based on some new techniques have been developed at the National Metallurgical Laboratory. In this paper, methods of spectrographic determination of boron in steel, aluminium in steel, magnesium in nodular cast iron, copper and magnesium in zinc base die-casting alloys and antimony in tin-lead non-antimonial solders in use at the N.M.L. have been outlined. Accuracy of such methods, type of spectrograph, source of excitation used and other conditions maintained to obtain reproducible results have been outlined in this paper.

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Analytical methods in micro-metallurgy

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IN this review salient features of the various procedures which have recently appeared in literature during 1960–63 have been discussed at some length also indicating in brief the effects of the elements, which when introduced in very small quantities into metals and alloys produce beneficial properties or modify them.

The occurence of the elements in the metallic materials being of much importance, the method of attack in opening the sample and the subsequent techniques for separating the elements from interfering substances are also considered before the actual determinations are discussed.

The discussions of the various procedures appear in alphabetical sequence of elements in (1) Iron and steel (2) Aluminium and its alloys, (3) Copper and its alloys, etc.

Special methods such as micro and ultramicro-techniques have not come into general use. Even the and in a somewhat conventional manner. The discussions covered here are as much based on analytical methods currently in vogue.

Although some of the procedures were originally devised for analysis of elements occurring as impurities in metallic materials their utility in the present context is realised and cited where appropriate.

The references cited in the case of some inaccessible literature were read only in the abstract form and given for completeness as well as for ready informatoin of analysis engaged in application of analytical methods in micrometallurgy projects and industries producing or using such materials.

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I, R. M. Krishnan, hereby declare that the particulars given above are true to the best of my knowledge and belief.

Sd/- R. M. KRISHNAN
Signature of Editor.

Dated 28th February, 1965.

Pearlite Free Structural Steels

J. A. Chapman
R. Phillips
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CONSIDERABLE research is now being carried out on the effects of reducing the carbon content in plain carbon-manganese steels to micro-metallurgical levels, at the same time introducing micro-additions of niobium and vanadium. The advent of oxygen steelmaking has made the manufacture of this type of steel commercially feasible with a reasonable prospect of economic viability.

Recent work[1, 2] has shown that a low carbon content in ferrite-pearlite steels is beneficial to toughness and weldability and decreasing the amount of pearlite has very little effect on the yield strength when the carbon content is less than 0·25%, although the U.T.S. is reduced.

Low carbon contents in air-cooled carbon steels, however, due to higher transformation temperatures, lead to coarse ferritic grain structures which are detrimental to yield strength and toughness properties. In low carbon steels, therefore, adequate means of grain refinement must be found if the full potential of such steels is to be realised.

Manganese lowers the transformation temperature and is beneficial to toughness in moderate amounts. Niobium and vanadium are excellent grain refining additions. Furthermore, if control is exercised during rolling, particularly on the finishing temperature, it is possible to obtain a refined grain size.

This reasoning lead to laboratory trials of low carbon (0·04%), high manganese (1·5—2·0%), niobium (0·06%) and vanadium (0·06%) steels in both the controlled rolled and normalised conditions.

Effect of carbon and manganese

The volume fraction of pearlite present in steels is controlled by the carbon level and up to about 20% has no significant effect on the yield stress[1, 2]. An increase of 1% volume fraction raises the Charpy V-notch transition temperature by 2—3°C, (according to the exact definition of transition used) at the same time increasing the U.T.S. by 0·3-0·4 t.s.i.[1, 2]

Increasing the carbon level has a marked effect on the ferritic grain size of air cooled steels after rolling to a given finishing temperature. Figure 1 illustrates that an increase in carbon from 0·05% to 0·15% reduces the grain size by about 1·5 mm$^{-\frac{1}{2}}$ (2 ASTM units) in a 0·8% Mn air cooled 13/16″ diameter round bar.

Weldability is considerably improved by reducing the carbon content because harmful transformation effects are avoided.

Manganese has a marked effect on refining the ferritic grain size in carbon steels for a given cooling rate. It also inherently improves the toughness over and above the effects which may be anticipated from grain refinement.[3] Phillips[4] found that an increase of Mn from 0·8% to 1·5% decreased the 40 ft lb. Charpy V-notch transition temperature at a given grain size by about 30°C. Manganese also contributes to the solid solution hardening by about 2 t.s.i. per 1% manganese level.[1]

Effects of grain size

Grain refinement increases the yield strength of plain carbon and carbon manganese steels by about 1·2 t.s.i. per mm.$^{-\frac{1}{2}}$ The rate of improvement may be drastically reduced in the presence of appreciable precipitation hardening.[5] An improvement in the Charpy V-notch transition temperature by at least 6°C per mm$^{-\frac{1}{2}}$ invariably accompanies grain refinement; thus there is a premium on producing a fine grain size.

Factors influencing grain size

Several factors can contribute to the production of fine grain size as rolled steels, viz. increased hardenability, heavy drafting in hot rolling, low finishing temperature and rapid cooling rates, the choice of which is generally dependent on the required finished thickness.

There is insufficient quantitative data on these factors but generally there is a greater opportunity to achieve a fine grain size in as rolled thin sections than in normalised steels. The latter, however, are generally finer grained than as rolled thick sections as currently produced.

The effect of finishing temperature on the grain size of experimentally as rolled 13/16″ diameter plain carbon steel rounds is shown in Figure 1;[6] the effects of increased hardenability may be adjudged from the grain refinement achieved in identically rolled Si-killed (0·24 C, 1·69 Mn) steel in which grain sizes of 17μ and 10·75μ were obtained in finish rolling at 950°C and 800°C.

In normalised steels, the ferrite grain size is closely related to the prior sustenite grain size[7] which is controlled by the volume fraction (f) of dispersed phases and their radius (r), the austenite and eventual ferrite grain refinement being controlled by the ratio f/r.[8]

Effects of niobium (vanadium)

Phillips et al.[9] found that a precipitation hardening addition of 0.03% Nb raised the friction stress (σ_i)* of 0.17C, 0.8 Mn by 3 t.s.i. when in the form of $\frac{13}{16}$″ rounds experimentally finished rolled at 950°C and refined the grain size by 3mm$^{-\frac{1}{2}}$, whereas 0.06% Nb for the same processing conditions gave similar grain refinement but

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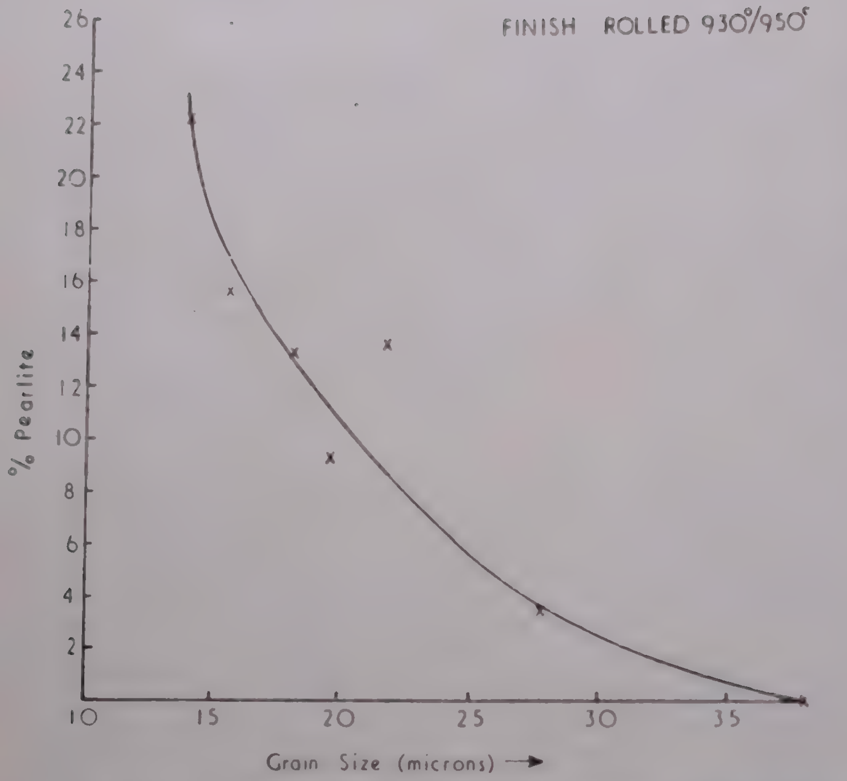

1 *The effect of carbon on grain size for a constant finish rolling temperature*

raised the friction stress by a further 3 t.s.i. More recent results[5], however, suggested the increments given in Table I.

TABLE I

%Nb	$\Delta\sigma_i$ (t.s.i.)
0·01	7
0·03	03
0·06	18

with Ky decreasing as σ_i increases.

Appreciable precipitation hardening may also be obtained with V additions particularly in the presence of high N-levels. The increase in yield strength ($\triangle\sigma_y$) at $d^{-\frac{1}{2}} mm^{-\frac{1}{2}} = 9$, found in experimental steels based on 0·17C, 0·8 Mn, are given in Table II.[2]

TABLE II

V%	N%	σ_y (t.s.i.)
—	0·007	—
0·06	0·006	3
0·06	0·010	4·5
0·06	0·014	6·5
0·06	0·022	9·5

Development of new high yield strength—tough steels

TABLE III

Steel	—	C%	Mn%	Nb%	V%	N%
1	S 155	0·039	1·52	0 052	—	0·005
2	V 585	0·013	1·5	—	0·07	0·02
3	S 132	0·049	1·91	0·061	—	0·011
	S 133	0·049	1·81	0·06	—	0·0145

Steels of the compositions shown in Table III were produced by vacuum melting Swedish Iron, electrolytic manganese and spectrographic graphite. The steels were rolled on the experimental bar mill to $\frac{13}{16}$" rounds, finish-

air cooled steels rolled to 950°C were also normalised at 900°C.

As rolled steels

The mechanical test data of the as rolled steels are presented in Table IV.

TABLE IV

Steel	Finishing Temperature (°C)	U.T.S.	L.Y.S	El.	R.A.	Ferrite Size (μ)	Transition Temperature (°C)
1	950	32·2	26·1	40·4	82·1	11·8	— 55
	850	31·8	28·3	46·1	84·0	8·09	—105
2	950	29·5	23·0	40·0	80·0	15·1	— 35
	750	33·0	30·0	30·0	74·0	11·5	— 54
3	950	36·15	28·65	37·25	79·95	7·85	— 21
	915	37·25	29·95	36·9	75·65	6·85	— 48
	880	35·8	30·35	40·4	80·9	3·79	— 90
	845	35·3	30·7	44·0	81·4	7·62/3·27	—105
	820	35·95	30·8	40·7	28·45	10·9/3·27	— 90
	780	36·1	30·75	41·1	78·5	11·0/2·97	— 68
	757	33·75	29·65	45·05	82·1	11·5/3·76	— 85
	725	35·85	31·8	38·3	81·7	9·8/3·62	— 64
	690	43·85	41·05	30·85	71·0	10·0/3·6	— 85

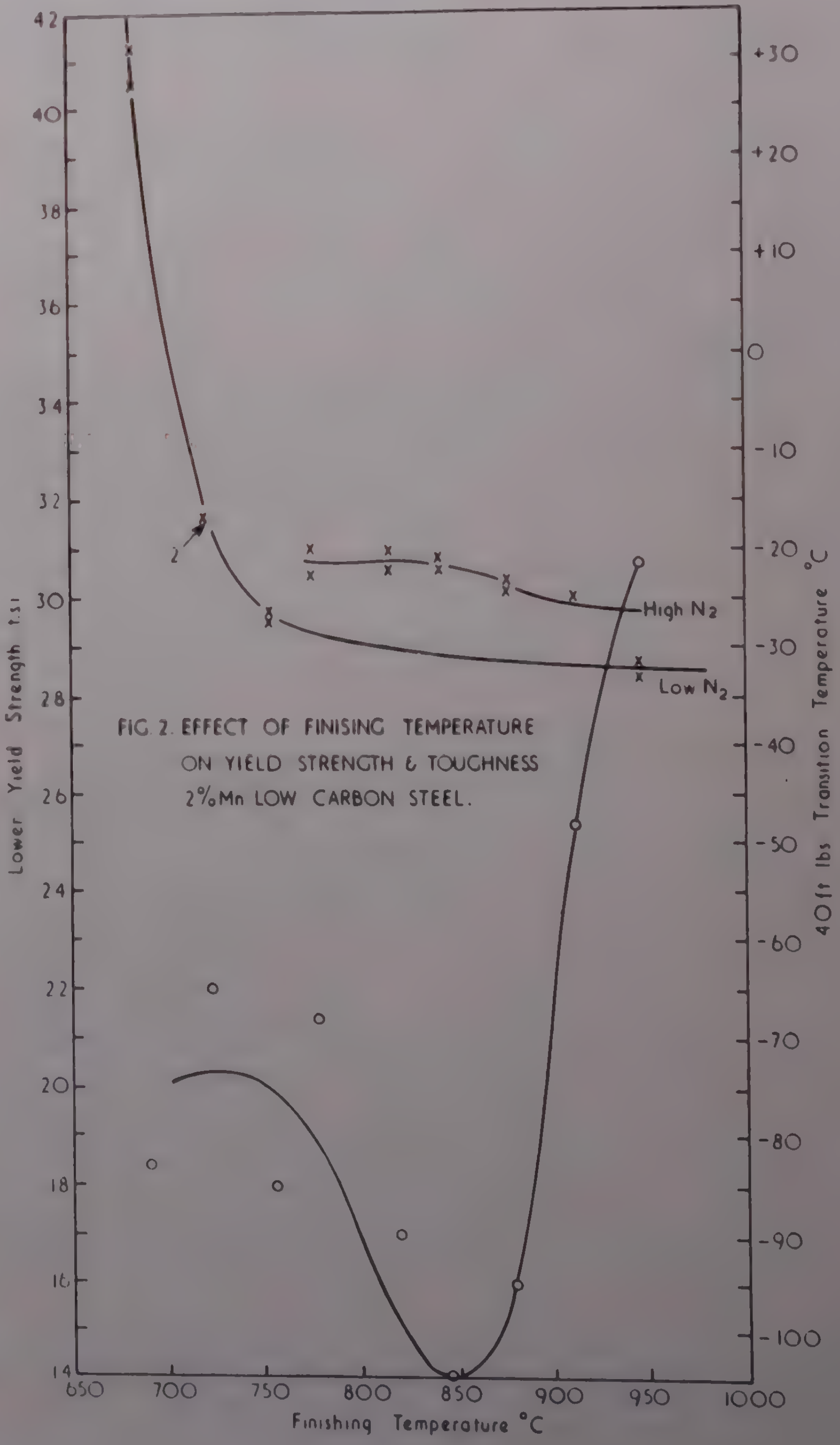

FIG 2. EFFECT OF FINISING TEMPERATURE ON YIELD STRENGTH & TOUGHNESS 2%Mn LOW CARBON STEEL.

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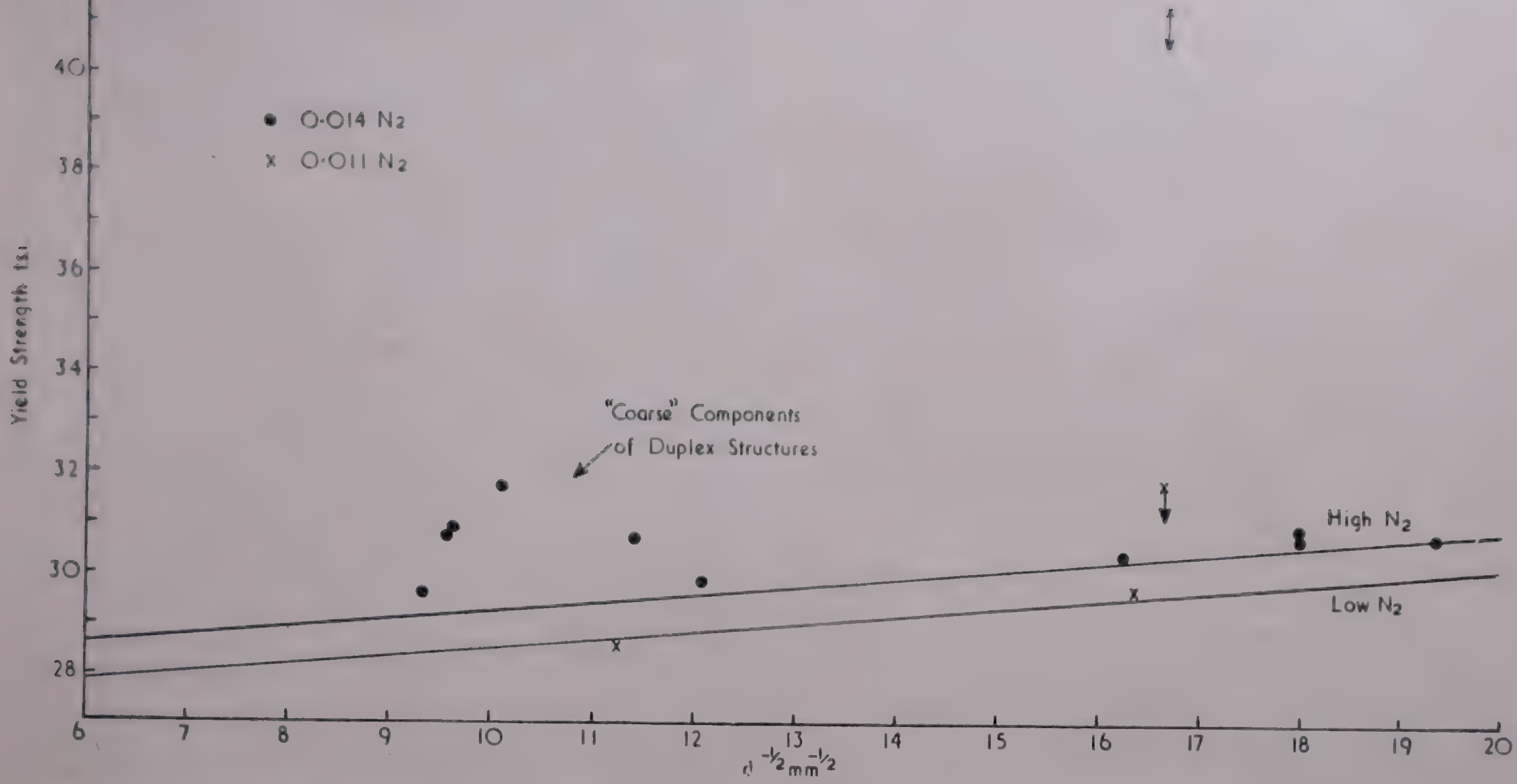
* From the Petch Relationship $\sigma_y = \sigma_i + K_y d^{-\frac{1}{2}}$ where the symbols have the usual connotation.



3 *Relationship between grain size and yield strength carbon for 2% Mn carbon steel.*

The yield strength and transition temperature of steel 3 are also shown as a function of finishing temperature in Figure 2.[5] Yield strength and transition temperature are shown as a function of grain size in Figures 3 and 4.[5]

Clearly the anticipated attractive combinations of properties have been achieved in the steels finished between 950°C and 750°C. Petch analysis of the results is rendered difficult by the occurrence of mixed grain sizes in steels finished at lower temperatures. However the following tentative points may be made :

(*a*) The grain size dependence of the yield stress is low and σ_i in steel 3 seems to be about 27 t.s.i.

(*b*) Both steels 1 and 3 show a more marked dependence of transition temperature on grain size than conventional plain carbon steels.

(*c*) Although the 1·5 Mn steel is much tougher at a given grain size (by-80°C) than the 2% Mn material, much finer grain sizes are obtained under given processing conditions in the latter material giving somewhat better combinations of mechanical properties.

(*d*) The U.T.S. is only 4 or 5 t.s.i. higher than the yield stress but the ductilities are high. This type of material may have particular advantages as a structural material since it has very ample capacity to flow to relieve a local stress concentration but in so doing would not harden or seriously embrittle.

Unexpectedly good combinations of properties were obtained when rolling the low carbon steels to finishing temperatures below 750 C. For example, rolling the 2% Mn, 0·06% Nb steel to finish at 690 C resulted in a yield stress of 41 t.s.i. and a brittle-ductile transition temperature of 70 C. Electron micrographs of thin foils of the low carbon steels show a marked increase in the dislocation density at the lowest finishing temperatures and the presence of very fine carbides intimately associated with the dislocations. Thus it would appear that a kind of dynamic strain ageing has occurred during the final pass or passes and that this mechanism confers a high strength increase with proportionately a very small rise in transition temperature.

Normalised low carbon steels

The normalised properties are given in Table V.

TABLE V

Steel	U.T.S. t.s.i.	L.Y.S. t.s.i.	El. %	R.A. %	Ferrite Grain Size (μ)	Transition Temperature (°C)
1	25·8	20·4	47·3	86	10·0	−110
2	24·0	18·0	51·8	85	11·6	−93
3	Not available					

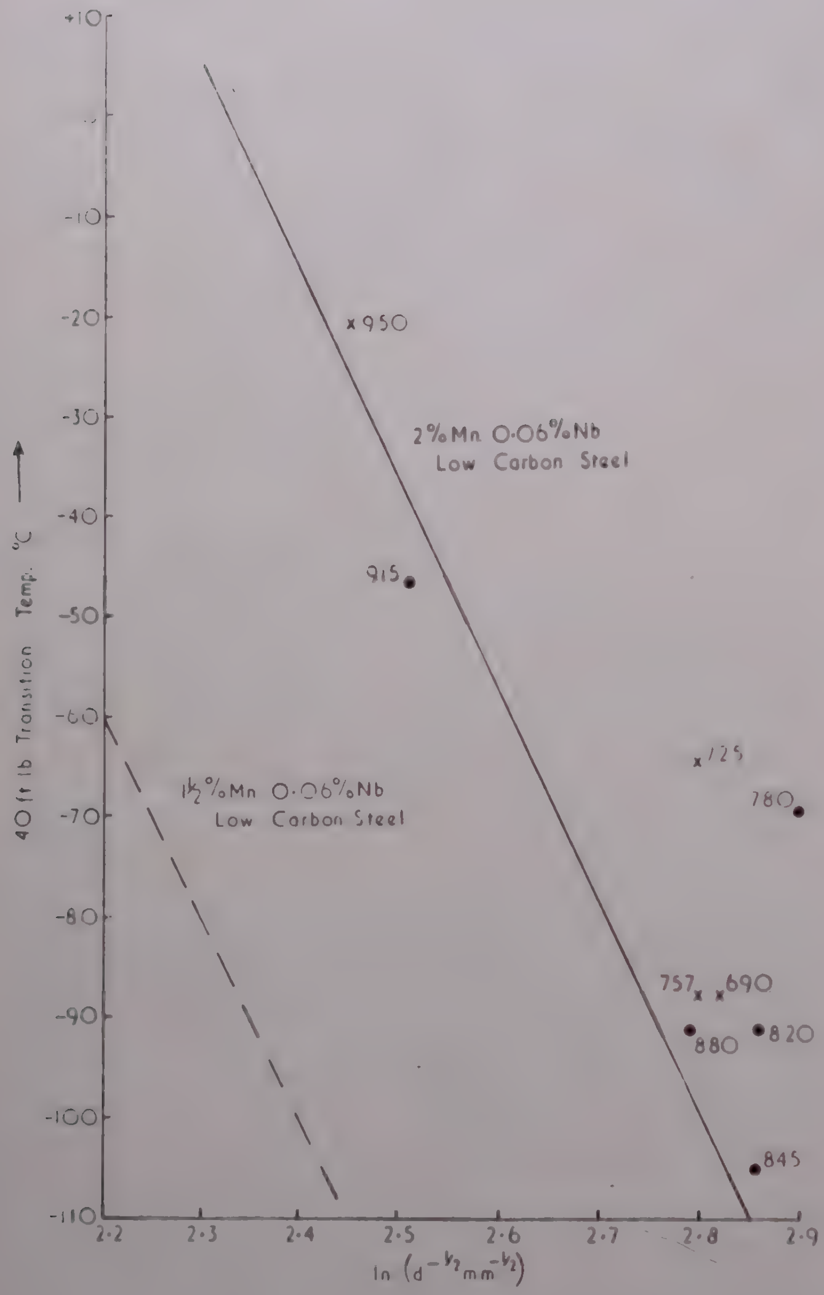
In the normalising treatment the finely precipitated carbides inhibit grain growth and the relatively high volume fraction of such carbides results in a very fine grain size. Precipitation hardening is, however, much reduced and the improvement in yield strength over plain C-Mn steel is largely due to the fine grain size. The low carbon steels are, however, very tough due to the absence of pearlite, the low friction stress and the fine grain size.

The absence of pearlite leads to brittle-ductile transition curves with a very high Charpy shelf energy >216 ft lb and a very narrow transition range. This applies also to the as rolled steels.

General discussion

An indication of the present position and future developments in conventional ferrite-pearlite steels may be assessed from Fig 5.[10] The yield strength-toughness combinations of the B.I.S.R.A. steels are also included (as points) on this diagram and their overall superiority in terms of yield strength for a given toughness or vice versa, is shown.

It remains, of course, to demonstrate how far similar properties to those obtained experimentally can be



4 *The relationship between grain size and 40 ft lb transition temperature for 2% Mn low carbon steel.*

ties are found to be worth any extra costs in manufacturing low carbon-high manganese compositions. Furthermore, alteration would be required to design codes and various standards to enable full advantage to be taken of high yield, high ductility tough steels with a high yield to ultimate ratio.

The optimum properties will most readily be achieved commercially in hot strip mill thin sheet products, black bar and light structural sections where current processing involves relatively heavy drafting at low falling temperatures.

Already, 1 000 tons similar to steel 1 has been manufactured by a B.I.S.R.A. member firm in the U.K. and rolled to 3/8″ plate. Yield strengths in the range 27 to 30 t.s.i. with transition temperatures less than −60°C were obtained. The weldability as defined by welded plate bend tests (R = 2T) was much improved.

The greatest requirement for higher strength tougher more weldable steels is in plates of 1″ thickness and above. The compositions discussed above, when processed to simulate the drafting, finishing temperature and cooling rates of the commercial production of heavier plates, do not have polygonal ferrite structures and have poorer properties. Thus there is a requirement for further work to develop compositions less sensitive to the details of hot working and to investigate how far the final drafting can be increased and finishing temperature decreased while keeping within shape, flatness, and surface finish requirements.

Acknowledgements

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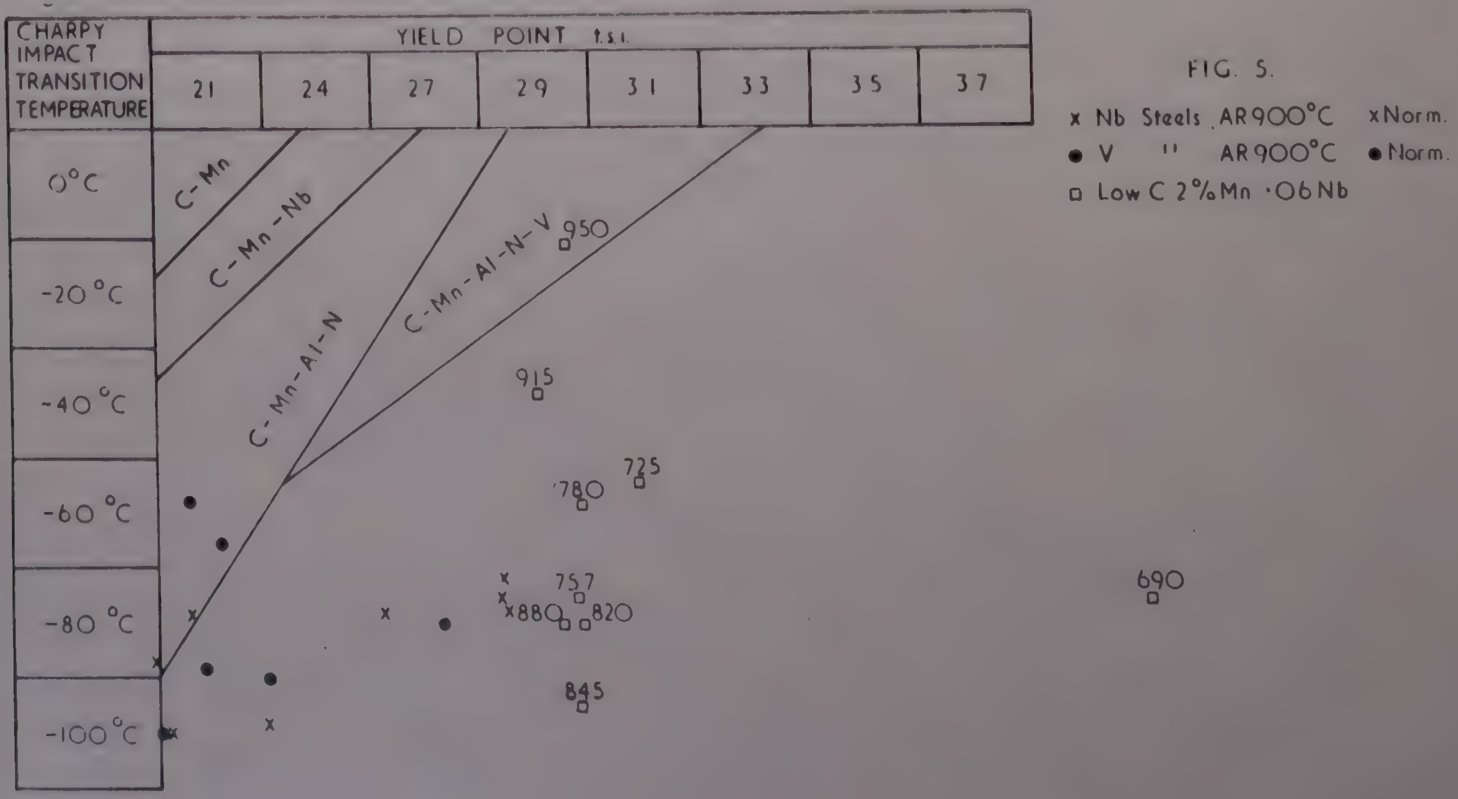

FIG. 5.

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Techniques for the Study of Micro-Phases and their Influence on Material Properties

D. Scott

It has been recognised for many years that minute quantities of certain elements and trace impurities unintentionally present in a metal can have disproportionate effects on properties.[1–5] An impurity in one metal, however, may well be an important alloying element in another; for example, boron is extremely harmful even in trace amounts in certain materials for use within nuclear reactors but small quantities of the same element may be deliberately added because of its highly beneficial effect in some steels and nickel base alloys. The effect of a small concentration of gases in metals may also be of critical importance; hydrogen embrittlement[6–8] has long been recognised whilst the major influence of nitrogen in carbon steel is now generally accepted.[9]

In materials, minor elements may be substitutional, interstitial or a separate phase, their distribution may not be homogeneous, and segregation at grain boundaries or surfaces may be important. To understand any deleterious or beneficial effects of minor elements it may be necessary to investigate their effects on many factors which can influence material properties. These include lattice binding, mobility of electrons, atoms, point defects and movement of dislocations. The effect of minor elements upon grain boundaries and the nucleation of phases is most important.

As our technological civilization expands, ever increasing demands are made on engineering materials To meet the stringent design requirements considerable research is carried out in an endeavour to substantially improve the mechanical properties of existing materials and to develop new alloys capable of meeting the requirements. In modern materials research the necessity of studying, in great detail, structural changes brought about by service conditions, the effect of minor elements on the changes and on the material properties requires the application of a wide variety of special investigational techniques and equipment. Specification from each technique enables comprehensive data to be obtained. In the National Engineering Laboratory many metallographic techniques are currently in use in materials research; several examples are cited later.

Use of electron microscopy and associated techniques

Although many refined techniques are available which extend the range of the modern optical microscope,[10–13] the resolution of the microscope and the nature of the specimen limits the magnification obtainable, and the electron mircroscope with its greater magnification is required to study fine-scale structural details of metals and alloys.[14–17] If the electron microscope were only limited by the same factor as its optical counterpart, i.e. the wavelength of the illumination, then its resolving power would be a small fraction of an angstorm unit (Å). However, spherical aberration and astigmatism caused by imperfections in the lenses set a limit, on currently available instruments, of several Å.[18, 19] Improvements may be expected to reduce this to one or two A.[20]

Direct examination

There is a considerable diversity of electron optical techniques of value for the examination of metals,[21–23] and the choice of method depends very much on the nature of the specimen and the fine-scale information required from it. Direct surface examination is useful[24, 25] but is limited to the examination of small specimens capable of being accommodated in the microscope. Although the use of glancing angle illumination may make interpretation somewhat difficult, direct examination by this technique may supplement information obtained from other techniques and may also verify the absence of suspected replication artefacts. Direct examination of conventional micro-specimens can be obtained with the scanning[26, 27] and emission[28] electron microscopes. In the scanning instrument the metal surface is scanned with a focussed electron beam and the detected secondary emission is used to modulate the brightness of a fluorescent screen scanned in synchronism to form an image. In the emission instrument the specimen is irradiated with a defocussed beam of electrons or ions, and the secondaries form an image by means of a lens system. Although better than optical methods, a serious disadvantage of direct methods of electron optical examination is the poor resolving power compared with that of transmission electron microscopy. For most general metallurgical work, replica techniques are used with the transmission instrument.

Replica methods

A large variety of materials and techniques can be applied to the replication of solid surfaces, [18,19-22;23-29] but what may be be a suitable method for one solid surface may not give the best results with another.

Replicas may be metal shadowed to improve contrast

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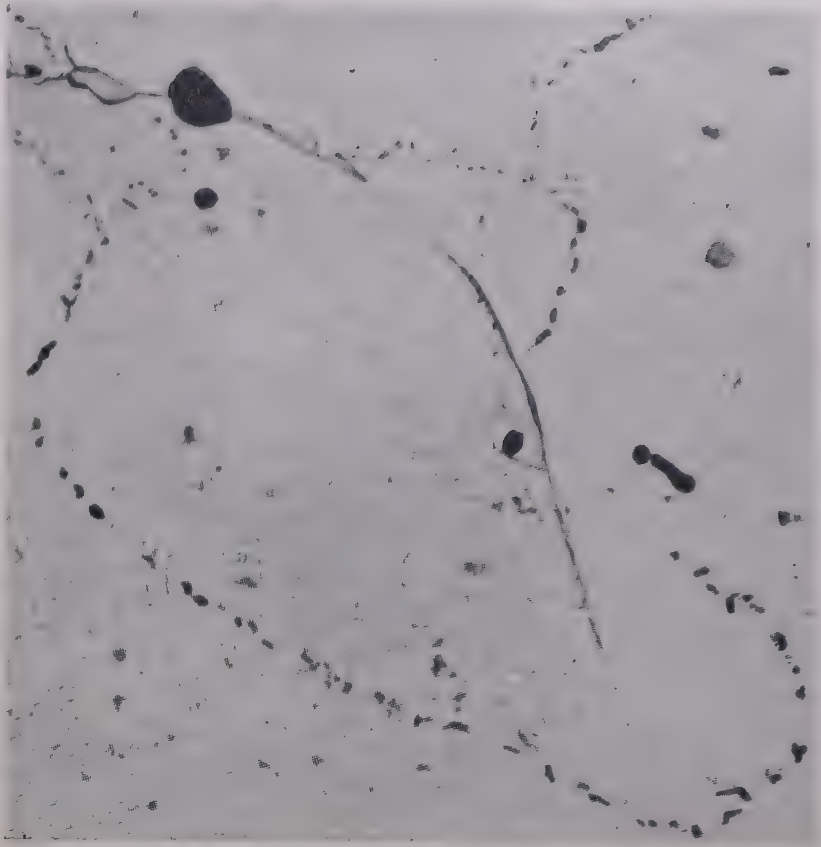
and render visible fine detail without confusing the interpretation of main structure. Simple, single-stage methods which produce negative replicas have generally been superseded by two-stage, positive replica techniques which reproduce surface features in their true perspective. The high-resolution carbon replica technique developed by Bradley[30,31] and various modifications of it have been found to be particularly effective.[32,33] Where other methods of investigation have failed, the electron microscope employing carbon replica techniques has been able to reveal difference in structure responsible for as much as a six-fold increase in tool wear during the machining of apparently identical ingots of leaded bronze bearing material;[34] fine oxide particles, present in the material of the bad ingots, were causing the trouble, Fig. 1 (× 14 000).

Fine details of micro-structure can be obtained from replicas but in order to determine complementary information regarding size, shape, composition and distribution of minor dispersed phases or precipitates, etc., carbon extraction replica techniques are used.[35,36] A direct carbon replica may be chemically removed from an etched surface by controlled attack of the material so that the removed replica retains the dispersed phases or precipitates attached to it in the positions occupied in the original structure. The crystal structure of the individual particles can be determined in the microscope by the use of selected area diffraction technique.[37] A tilting and rotating stage allows crystallographic axes of crystalline particles to be positioned in preferred orientations relative to the electron beam so that the most suitable diffraction pattern for identification is obtained.[38, 39] Several crushed extraction replicas may be used to provide powder material for identification by X-ray diffraction of fluorescent analysis.[40]

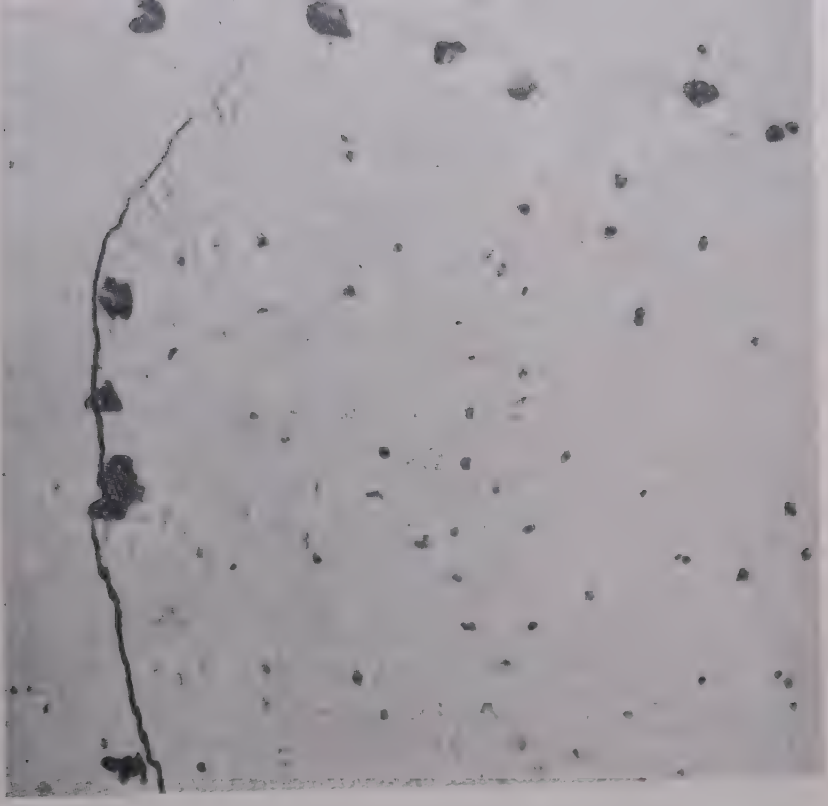
The role of electron micoroscopy of extraction replicas is well illustrated in the field of creep-resisting materials where alloy phases have been detected at different stages of heat-treatment and service, and it has been possible to associate changes in mechanical properties with changes in the nature of minor phases.[41,42] An example is the slight coarsening of AlN precipitate in aluminium-killed 1% manganese pressure vessel steel, Fig. 2a (×6 500), but greater coarsening of SiN in silicon-killed similar steel. Figure 3a (×16 000) due to high temperature stress relief; this may be interpreted as evidence of 'active nitrogen',[43] present in solution in normalised silicon-killed steel, providing dislocation locking and superior creep resistance of this steel when subjected to lower tempertature stress relief. Selected-area diffraction confirmed that the nitrides formed wear



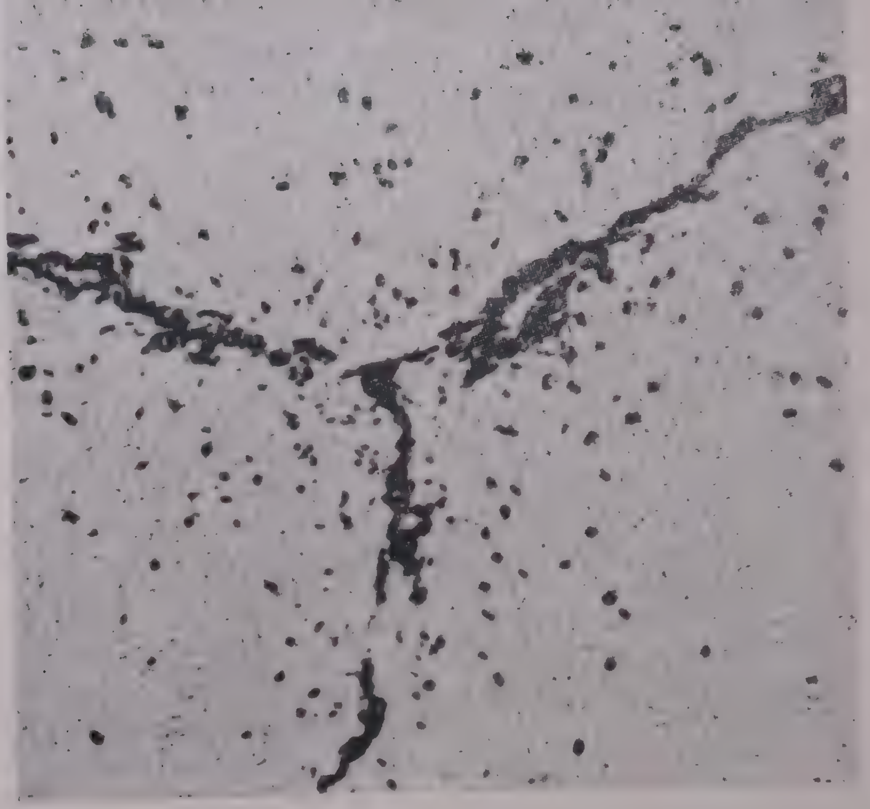
2 *a* *AlN precipitate in aluminium killed 1% manganese pressure vessel steel. Carbon extraction replica.* *×6 500*

1 *Fine oxide particles in leaded bronze bearing material.* *×14 000*

2 *b* *Electron diffraction pattern of AlN.*



3 a *Sin precipitate in silicon killed 1% manganese pressure vessel steel. Carbon extraction replica.* *16 000*

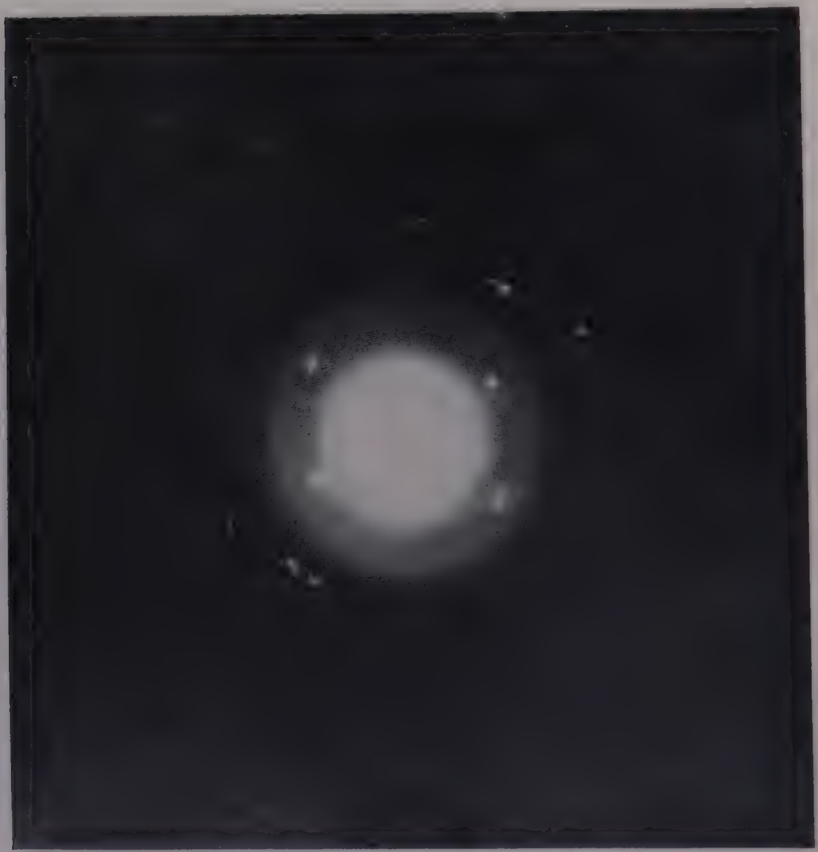


4 a *Grain boundary precipitate and segregation of large matrix precipitate in the vicinity of the grain boundaries of Nimonic 90. Carbon extraction replica.* *×6 500*

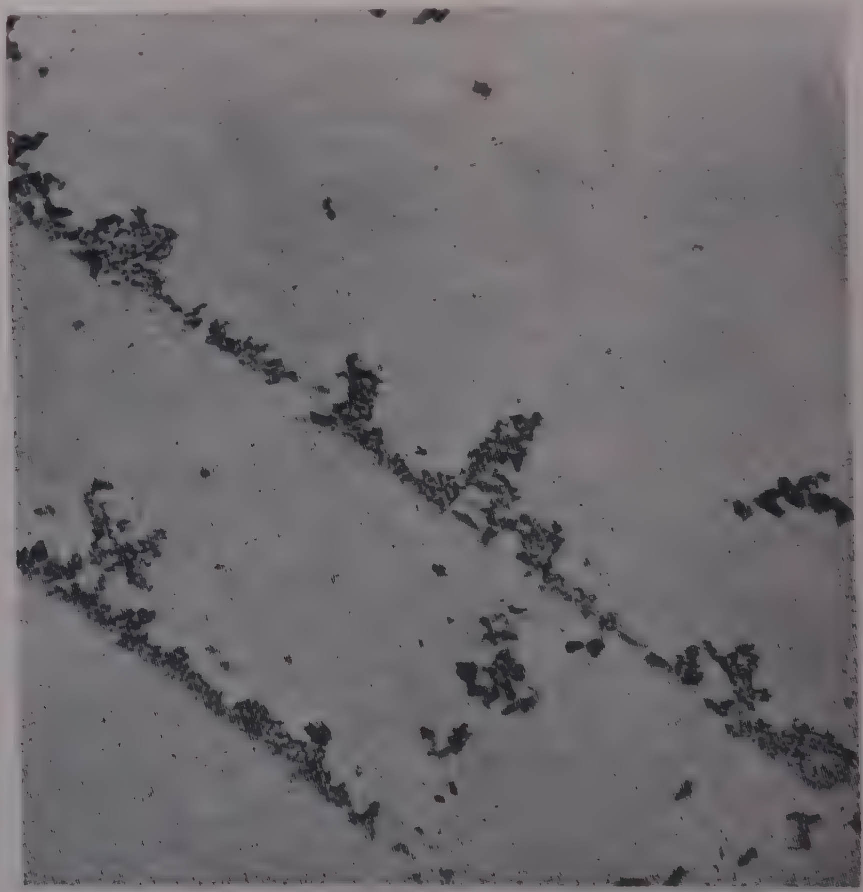
AlN, Fig. 2b, and SiN, Fig. 3b, as suggested by Arrowsmith.[44] No evidence of α or β Si_3N_4 was found.[45] Other workers have studied the occurrence, morphology and identity of nitride precipitates in iron and steel using extraction replicas.[46,47]

Structural changes observed in Nimonic 90 by electron microscopy and studied by electron diffraction were correlated with the variation in creep 'activation energy' and the phenmenon of negative creep in a sample of this material. Material tested at higher temperatues showed a somewhat heavier grain-and twin-boundary precipitate of $C_3r_2C_6$ frequently in the from of triangular platelets whilst the matrix showed a segregation of large precipitates of $Ni_3(TiAl)$ in the vicinity of the grain boundaries, Fig. 4 (a and b) (×6 500).

Extraction replicas have been used extensively in studying and minor phases in various types of steels[48-53] and other alloys.[15,54,55] For example, it has been shown that secondary hardening of a CrMoV steel depended



3 b *Electron diffraction pattern of Sin.*



4 b *Percipitation on Twin boundaries of Nimonic 90. Carbon extraction replica.* *×6 500* upon dispersed fine carbides in the ferrite grain,[56] whilst in the field of stainless steel and heat-resisting alloys structures and phases have been identified to enable correlation between structure and mechanical properties[15,16,54,55,57-60] to be achieved.

Replica techniques have provided fine-scale information of use in the elucidation of failure mechanisms which initiate on a sub-microscopic scale. In the study of fatigued metals it has been shown that cracks or fissures, which develop within slip bands, can propagate to cause failure.[61,62] This phenomenon can be related to the formation of extrusions and intrusions.[63,64] It has been shown that the rupturre life of certain creep-resistant materials depends upon the rate of development of micro-cracks at grain boundaries,[60] whilst cracks originating around hydride particles in zirconium alloys contribute to hydrogen embrittlement.[65]

Thin foil techniques

The behaviour of soil materials demands to a large extent on defects in the atomic arrangement in the crystals of which solids are composed. Mechanical properties such as strength and plasticity are largely determined by crystal imperfections, and thin-foil transmission electron microscopical techniques afford a method of studying these imperfections[22,23,66,67,68] and the effect of dispersed minor phases on their behaviour. These techniques have introduced a new quantitative micro-metallurgy.[69] Following the earlier work of Heidenreich.[70] Castaing[71] and Eirsch et al[72,73] Bollman[74,76] showed that foils suitable for examination in transmission by high-resolution double-condenser electron microscopes could be prepared by electro-polishing methods. Suitable foils can now be prepared by a variety of methods[22,23,67] following sectioning of the specimen by electro-polishing,[75,76,77] chemical thinning,[72,78] microtoming[79] or jet-machining,[80] etc.[22,23]

Thin film techniques besides providing experimental confirmation of fundamental concepts of dislocation theory[72,75,81] are uniquely suited for observing various types of structural defects including antiphase domains and boundaries,[82] features of ordering,[86] vacancies,[84] various types of dislocations.[66,85,86] stacking faults[87] and twinning[88]. Figure 5 (a and b) (×30 000) show, respectively, dislocations in heavily worked 18/8 stainless steel, and twinning in annealed 18/8 stainless steel. The crystal lattice of suitable specimens can be resolved,[89] and use of moire' fringe techniques can give enhanced magnifications.[90]

5 a Dislocations in a thin film of heavily worked 18/8 stainless steel. ×30 000

5 b Twinning in a thin film of annealed 18/8 stainless steel. ×30 000

Precipitation phenomena and phase transformations can be studied to considerable advantage by thin film methods.[91] Enhanced contrast from diffraction effects renders visible particles too small to be revealed by etching. Use of a goniometer stage enables contrast effects to be controlled, and with selected-area electron diffraction it is possible to determine the identity, form, crystallographic orientation and distribution of phases present. Strain fields, which develop around Gunier-Preston zones, have been detected and G–P zones of one atomic layer thickness and about 50Å in diameter have been observed.[92] The interaction of dislocations with precipitate particles has been studied.[93]

Fractography

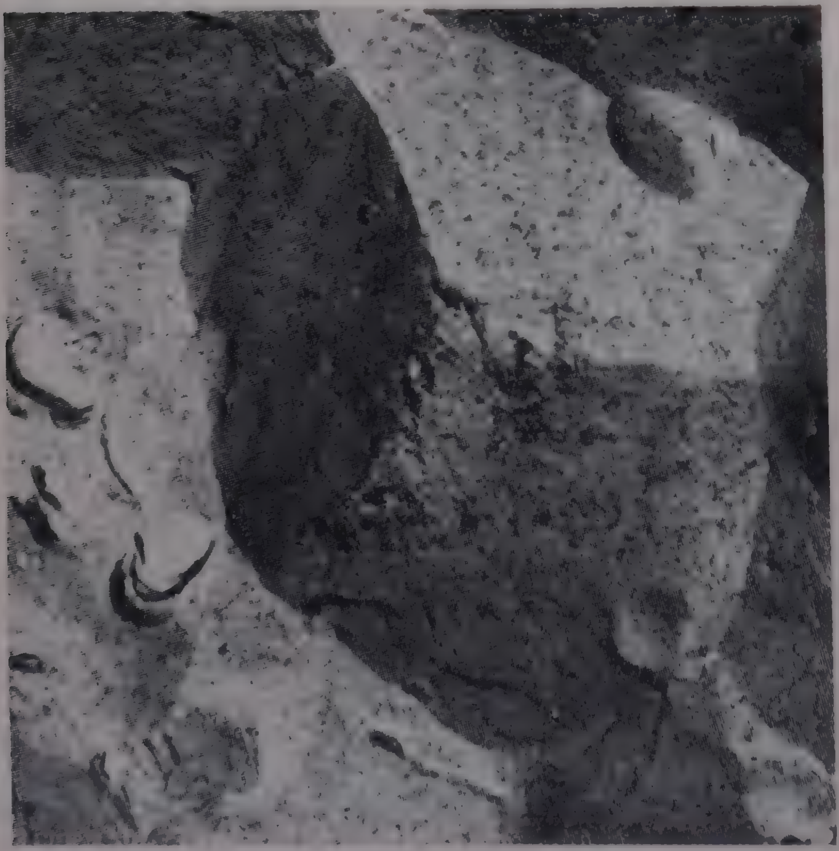
Intergranular weakness which may cause a potentially high strength alloy to be brittle and weak can often be correlated with precipitation at grain boundaries or with soft denuded zones adjacent to grain boundaries. Electron microscopy has enabled fundamental information on these phenomena to be obtained.[91] The great depth of focus of the electron microscope can be profitably used to examine rough surface such as fracture surface not suitable for examination by optical methods at high magnification. Besides giving information regarding the type of failure, electron micro-fractography may also yield specific information relating to material structure.[22,23,41,94-96] Various techniques are available for the replication of rough surfaces, ranging from direct carbon to a variety of two and three-stage methods.[22,23] In the examination of intergranular features the electron microscope allows grain boundaries to be examined two-dimensionally and reveals in great detail the three-dimensional appearance of any grain boundary precipitate. Minor elements may concentrate at grain boundaries to cause intergranular failure and brittleness, e.g. chromium sulphide in iron-chromimum alloys, and thin platelets of manganese sulphide in low-alloy steels.[97,98] Hydrogen embrittlement can effect the fracture mechanism and fracture appearance:[99,100] this phenomenon has been associated with intergranular fracture, sometimes along prior austenite boundaries.[101,102] Figure 6(× 18 000) shows intergranular fracture of a ball bearing in which hydrogen embrittlement, from lubricant causes, was a contributory factor in premature failure. Normally the useful life of ball bearings and other rolling mechanisms are limited by surface disintegration, pits being formed by a process having fatigue characteristics.

Dynamic electron metallography

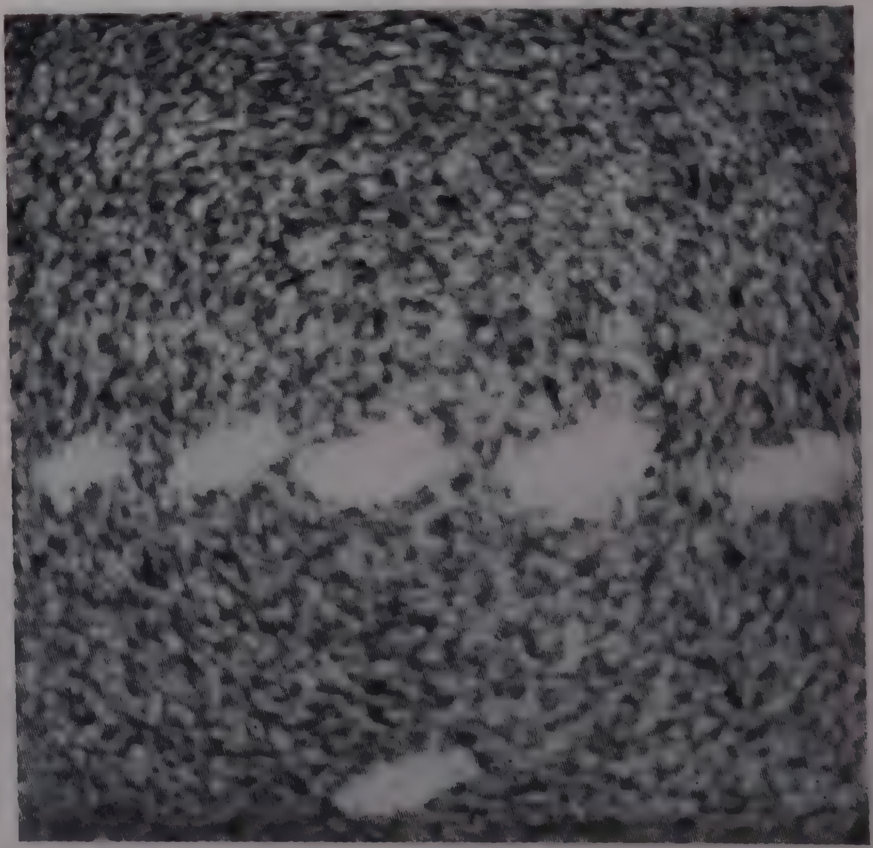
There is an increasing tendency for the metallurgist to endeavour to mount his laboratory, as it were, within the electron microscope in order to study transformations and mechanisms as they occur. Since many changes in metals, including those affected by minor phases, are temperature-dependent, the use of heating and cooling stages can be useful in following changes in thin films.[22,23,103,104] The formation of precipitates on ageing can be studied by this method. The solution treatment and precipitation hardening of aluminium alloys have been studied using a heating and cooling stage with sequential and cine-photography to record the changes.[105] Straining devices[106,107] can be used and may be combined with heating, cooling, and tilting stages in order to study plastic deformation, the movement of dislocations, and their interaction, and the effect of minor phases on these phenomena.

Although use of extraction replica and thin film techniques with electron microscopy enables the isolation and identification of fine precipitates and phases, many metallurgical problems are due to solution segregation particularly on a micro-scale. The technique of electron probe X-ray micro-analysis initiated by Castaing[108, 109] has now been developed[110–112] to provide commercially-avaiable instruments for studying micro-segregation effects, composition of inclusions, denuded or enriched zones adjacent to grain boundaries or around particles, and the composition of scale. Generally, in these instruments, a finely focused electron beam scans the specimen, and the elastically scattered and emitted secondary electrons are collected, passed through an electron multiplier, and displayed on a cathode ray tube in synchronism with the scan to provide a visible image. The characteristic X-ray emission from a selected element may be counted and the signal from the counter used to modulate the beam scanning the cathode ray tube to provide an image displaying the distribution of the element in the surface scanned. An approximate quantitative analysis is carried out by recording the intensity of emission at a point usually about one micron cube and comparing this with the intensity of emission from the pure element or standard, when irradiated under the same conditions. Correction factors are usually required.

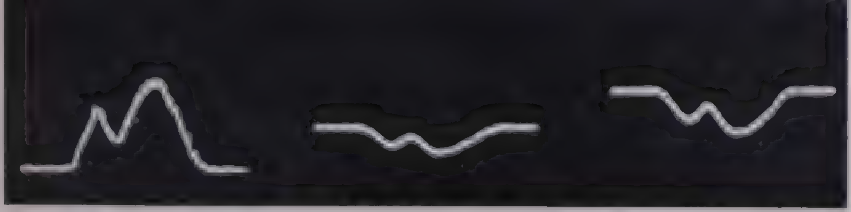
The potentialities of the technique have been well illustrated. The surface segregation of 'tramp' elements leading to the hot-shortness of mild steel has been investigated,[113, 114] and the segregation of lead in a free cutting steel.[114] Selective oxidation during scaling, segregaiion in banded structures, and diffusion in alloys at elevated temperatures have been studied.[115] The technique has been used to establish the composition of sulphide inclusions detected and identified by optical methods and has shown that iron sulphide rarely contains any manganese but that manganese sulphide



6 *Intergranular fracture of hydrogen embrittled ball bearing steel. Two stage perspex carbon replica.* *×18 000*



7 *a X-ray image of sulphur distribution associated with inclusions in Monel.* *×7 750*

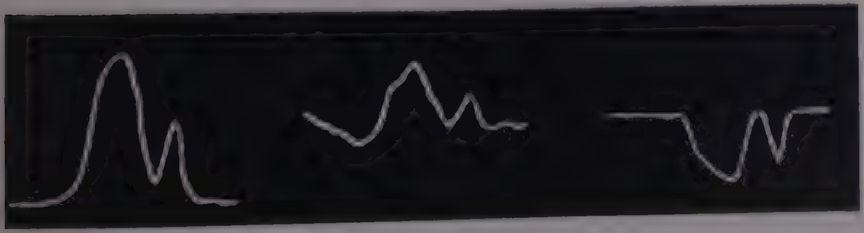


7 *b Line traces for sulphur, copper and nickle across inclusions.*

actually contains more iron than manganese.[115] An 'Atlas Metallographicus' of non-metallic inclusions has been compiled following work on the identification of inclusions in steel.[116] It has been shown that micro-segregation of residual elements, such as Ni, Cu, and Sn, is confined to the austenite boundaries near the surface.[117] Many applications covering nucleation, denudation and enrichment phenomena have been reported.[17, 118, 122]

Figure 7a shows the X-ray image of sulphur distribution associated with inclusions, and Fig. 7b the line traces for sulphur, copper and nickel over the same area of Monel metal. Figure 8 shows the identification of precipitate in Ni-hard material, Fig. 8a being the electron image of the precipitates and Fig. 8b being the line traces for Mo, Cr and Fe over the two precipitates present, showing them to be mixed Mo and Cr carbides.

8 *a Electron image of precipitates in Ni-hard material.* ×15 500



8 *b Line traces molybdenum, chromium and iron across the precipitates.*

Assessment of the effect of micro-phase by fitness for service tests

The absence of any recognized general code of practice, well established specifications, or standard test procedure for evaluating materials for specific advanced design requirements means that suitability can be reliably established only by performance in practice. As full-scale testing is expensive as well as time absorbing, accelerated simulated service testing is a valuable means of obtaining information on the behaviour of materials subjected to conditions representative of those which apply in practice; it is also a means of assessing the effect of minor elements on the performance. The effect of the steelmaking process[123] and the role of hydrogen[124] on rolling contact fatigue life have been assessed by the simple, rapid, rolling four ball test; the effect of different types of inclusion on ball bearing steel performance by the Unisteel fatigue machine,[125] and the effect of residual elements on ball bearing fatigue life by Laboratory test rigs.[126]

Discussion

The successful investigation of the effect of micro phases in metals and alloys depends largely upon the ability to isolate and recognise significant features and to isolate and identify essential phases in the micro-structure. The electron microscope, with its multiplicity of techniques, allows complete investigation of any structural feature which could significantly influence material properties. Replica and thin-film techniques are available which have resolving powers equal to those of the best available microscopes. If a micro-phase can be isolated by etching, replica techniques are the simplest to use, and identification of micro-phases is possible by electron diffraction or x-ray diffraction of extraction replicas. Thin-film techniques increase the scope and potentiality of the transmission electron microscope and allow growth mechanisms of micro-phases to be studied in relation to lattice defects; however, they present considerable difficulties in detailed interpretation. Whilst there is an increasing tendency to study thin films in dynamic conditions, and the use of heating, cooling and straining stages may appear to be advantageous, doubt exists as to extrapolation from thin films to bulk material. The development of high voltage electron microscopes [127–130] may offer opportunities for examining thicker specimens, but in the present state of knowledge of electron lenses the law of diminishing returns operates, and it appears that these instruments will remain economically prohibitive in the near future. Thermionic emission electron microscopy may possibly be developed to enable bulk specimens to be examined and to elevate hot stage microscopy techniques into the electron optical range [131],[132].

The electron probe X-ray micro-analyser is a powerful metallurgical tool for the study of micro-phases and minor elements, particularly of solution segregation on a micro-scale. Although still primarily a qualitative instrument, accurate quantitative analyses procedures are rapidly being established.[133] The application of the technique to the important elements of low atomic number, such as carbon, nitrogen and oxygen is progressively being developed.[134],[135] The use of ions for micro-analysis has been demonstrated.[130] Employing a a low-intensity image convertor instead of a fluorescent screen, the image is superior to that obtained from scanning; the penetration is only 10Å; the method is well adapted to the analysis of light elements and oxides, and the resolving power is down to 20A. As isotopes have different characteristic ions, it is possible to analyse for isotopes and it is possible to progressively etch and analyse successive layers of a bulk specimen. Useful attachments are available to enable limited probe analyses with the conventional electron microscope.[137] The development is well underway of specialised instruments combining scanning, transmission electron microscopy, diffraction and probe analysis to enable as much information as possible to be extracted from a single specimen.[138–140] A conference dealing with these non-conventional instruments has been arranged.[141]

In conclusion it may be stated that techniques are available to disentangle the efforts of minor constituents and phases from the complexities of practical materials, to facilitate a basic understanding of their influence, and to allow a qualitative explanation of the mechanical behaviour of metals in terms of their micro-structures. Use of all available techniques of investigation of microphases enables comprehensive information to be acquired to bridge the gap, in detailed understanding, between pure materials, that are amenable to fundamental study, and complex alloys which are often dependent upon minor phases for particular properties required by modern technological development.

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Rare Earth Metals in Stainless Steelmaking

L. Nemethy

AFTER the Second World War the production of Stainless Steels took a big step toward mass production. With the war time nickel shortage over, the production of austenitic stainless steels reached peaks never thought of, due to the development of numerous new applications such as: automobile trims, cooking utensils, architectural applications and food processing equipment. Several steel works competed for the growing market with many newcomers. The steelmaking practice itself underwent considerable changes. The use of stainless scrap was made possible by the introduction of oxygen; chromium-recovery was considerably improved by understanding the thermo-dynamical characteristics of the oxidation phase of steelmaking; furnace sizes were increased to 100 ton units and larger for melting stainless steels, and the introduction of high-accuracy immersion thermocouple and fast chemical analytical methods by the adaptation of spectrograph and X-ray analysis made steelmaking condition standardized and more scientific.

A number of special austenitic stainless grades were developed for special applications, such as the extra low carbon austenitic grades, molybdenum bearing stainless steels, special austenitic steels for cold-heading and welding wire applications, etc.

Despite the many improvements, the processing of stainless steels presented some difficulties, particularly during the initial stage of hot working. The high cost of processing rejects necessitated a thorough investigation of the contributing factors, but no safe procedure was found yet to overcome the difficulties.

With increasing furnace sizes, ingot sizes have been increased also. The early narrow strip mills have been replaced by modern wide stripmills upto 1·5 m width with coil weight up to 15 tons. Necessarily the casting of large slab-ingots became more and more into existence. The introduction of continuous casting process improved production rates, yields and overall economics but made very little change concerning the metallurgical problems of phase-changes, segregation, grain-boundary effects, etc.

The concept of 'Stabilized Structure' was developed and chemical balance was aimed for between ferrite and austenitic forming elements so that the formation of 'mixed' or so-called 'duplex' structure could be eleminated at any temperature. The understanding of multi-component alloy systems is still very limited and the practical difficulties experienced in the hot-working of austenitic stainless steels were expected to be eliminated by some 'minute additions' which were thought to have an ultimate improvement, and expensive experiments have been conducted.

Such a 'trial and error' rush was the application of rare earth metals in the 1950's through a number of years in United States and Canada without bringing a satisfactory solution to the problem of hot-workability. The availability of rare earth metals became a temptation for most stainless steelmakers during the last decade, yet years of investigations and trials failed to bring a solution to this problem. The North American experience was rather disappointing but one must admit that the related publications did not cover the whole picture.

Recently, Savitskii et al[1] reported on the numerous advantages of using rare earth metals for stainless steels, claiming the following improvements:

1. Increased fluidity of molten metal.
2. Reducing the oxygen content of steel.
3. Reducing sulphur content of steel.
4. Raising high temperature tensile strength.
5. Increasing ductility.
6. Improving hot workability.
7. The nickel content can be reduced yet maintaining a chemically-balanced composition for austenitic stainless steels.
8. Improved corrosion resistance.

These claims are not in agreement with North American experience and it seems to be in order to analyze the problem to some depth. It is true that rare earth metals are known as a group of elements for over a hundred years. It is also true, however, that more knowledge was gained during the last 5 years than during the preceding period. The Lanthanides became available in pure form due to such modern separation techniques as ion-exchange and liquid-liquid extraction at a reasonable cost. Binary alloy systems for almost all rare earth metals (with some more common metal) are known to-day, giving valuable information on possible phases, transformation temperatures, etc., which were not available 10 years ago when most of the experimental work was done in North America in connection with rare earth metals in stainless steels.

Crystal structures of numerous rare earth common metal binary systems are also known to-day, providing another important tool for the metallurgists for approaching alloy systems and the evaluation of certain properties.

In the following, the available technical cost and application data will be summarized.

Survey of literature

While several papers and books covered rare earth alloys since 1935—Hansen;[2] Janecke;[3] and Rolla et al;[4] the

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first reports covering the application in connection with ferrous alloys are relatively new. Knapp and Kolkcom[5] reported on the use of Lan-Cer-Amp alloy in connection with stainless, tool and other steels. These authors claimed sulphur and nitrogen removal (alloying 0·75-6 lbs of Lan-Cer-Amp per ton of steel) increased impact values, increased reduction of area, better corrosion resistance, better hot and cold working properties on stainless steels, improved workability in tool steels, and improved electrical properties in silicon alloyed electrical steels. Although they achieved some improvement in sulphur content, they did not claim it as a major function of Lan-Cer -Amp addition. It was also pointed out by the same authors that rare earth metals have a very high hydrogen solubility, that they form rare earth carbides, (R E C_2) and form very stable refractory oxides.

Burgess and Woodward[6] and Zieler's[7] early work on cleanliness failed to show any improvement when using rare earth additions.

Post-Scheffstall and Beaver[8] presented the first comprehensive paper directly related to rare earth in stainless steels. Their principal object was to improve the hot workability of austenitic stainless steels. They found that rare earth metals have been effective in promoting and improving the hot-workability of austenitic stainless steels.

The hot workability problems were attributed by the above authors to the following factors :

1. Contamination with elements such as lead, tin and silver.
2. Insufficient carbon in the charge during melt-down.
3. Unbalanced chemistry conducive to the formation of ferrite.

The above observations have been verified beyond doubts by others as well.

The "Cone-Test" for forgability developed by them was a genuine test to evaluate ductility during hot-deformation. They concluded that the necessary concentration of rare earth addition can be determined experimentally but they could give no clear explanation on the deoxidation effects or other benefits of rare earth additions. They pointed out, however, that some of the benefits obtained were due to a certain amount of deoxidation in the bath which was accompanied by a marked increase in the fluidity of the molten metal. Most of the steel used in connection with their work was made in an AJAX induction melting ; obviously this melting practice is altogether different to basic arc-melting which is mostly used for the melting of austenitic stainless steels to-day. Their rare earth addition was 2 lb per ton. Their AISI 316 experiments, however, were carried out in basic arc heats and they concluded that when austenitic steels are made in an arc furnace, half the amount of rare earth is producing the same improvement as compared to induction melting. For most of the work they used "Mischmetal" in 2–8 lbs. per ton quantities.

While the above authors concluded that rare earth metals are effective in improving the hot workability of austenitic steels, they have not presented numerical values for most of the properties investigated. However, their conclusions are of significant importance because they were able to demonstrate actual improvement in hot workability, and have given specific values for the rare earth concentration in order to improve hot workability.

The Molydenum Corporation of America has also done some work on AISI 310 stainless steels and other conclusions have been made.

Schwartzbach and Sheehan[10] investigated the effect of rare earth addition in connection with the impact propesties of SAE 4 330 steel. Their tests indicated that transverse impact properties of 4 330 steel were improved when rare earth metals were added.

As it can be seen from the above, by the early 1950's, the ground work has been laid for a full scale industrial application of rare earth due to the considerable improvements claimed.

Amongst a number of North American steel plants, ATLAS started full scale investigations as early as 1951. Commercial heats of AISI 308, 309, 310 and 316 heats have been treated with 'Mischmetals' and 'Rare Earth Fluorides' or oxides.

The 'Mischmetal' had the following composition :

Ceriumm	75%
Lanthanu	10%
Neodymium	8%
Praesodymium	3%

Barnhardt[11] summarized the early ATLAS experiments in the following :

1. Gardes investigated were-AISI 304, 316, 308, 309, 310, 317 and 330.
2. Investigation covered hot workability, grain size and cleanliness.
3. The effects of 4–8 lb of rare earth addition as 'Mischmetal' were as follows :

(*a*) AISI 308—16″ ingots of 12 ton heats melted in 12 ton basic electric arc furnace showed poor hot workability with or without rare earth addition.

(*b*) AISI 309—16″ ingots of 12 ton electric arc furnace heats showed some improvement with rare earth addition and balanced chemistry.

(*c*) ATLAS St. 309. This grads has an unbalanced chemistry. Rare earth addtions failed to improve hot workability.

(*d*) AISI 310—Rare earth additions improved hot workability.

(*e*) AISI 316—A total of 14 heats of 12 ton size were melted with 4 lbs. per ton of rare earth addition. The hot workability showed no improvement.

(*f*) AISI 317—Addition of 4 lbs. rare earth per ton of steel showed no change in hot workablility of this grade of steel.

(*g*) AISI 330—Addition of 4 lb per ton of rare earth per ton of steel showed only very slight improvement.

The chemical composition of the above grades is shown by Table I.

TABLE I Chemical composition of austenitic stainless steels investigated by Atlas Stesls Company

	Chemical Analysis							
	C	Mn	P	S	Si	Cr	Mo	Ni
AISI $ 308	·06	1·50	·030	·025	·25	20·00	·40	9·50
	max.	2·00	max.	max.	·50	21.50	max.	10·50
AISI $ 309	·15	1·00	·045	·030	1·00	22·00	—	13·00
	max.	2·00	max.	max.	max.	24·00	—	15·00
AISI $ 310	·10	1·50	·018	·025	·60	26·50	·40	21·00
	·15	2·00	max.	max.	max.	27·50	max.	22·00
AISI $ 316	·08	1.00	·045	·030	1·00	16·00	2·25	12·00
	max.	2·00	max.	max.	max.	18·00	3·00	14·00
AISI 317	·08	1·00	·045	·030	1·00	18·00	3·00	13·20
	max.	2·00	max.	max.	max.	2 ·00	3·75	15·00
AISI 330	·15	1·00	·045	·030	1·00	14·00	—	33·00
	max.	2·00	max.	max.	max.	16·00	—	36·00

Heats made with rare earth addition were no cleaner than heats made without, and no difference was found in grain size either.

Other US stainless steel makers found the same controversial results. Although a number of others reported on progress and cost savings over the years, and rare earth producers tried their best to promote their products, the addition of rare earth metals has been almost entirely discontinued in North America by the early 1960's, and it has been confirmed by the authur's survey in 1964.

Savitskii et al[1] findings and their publication in 1963 is, therefore, of concerned interst. The rare earth science, thanks to numerous investigators in the USA, Canada, UK, India, Germany and USSR, who made a greate progress over the past 10 years. The question is now how can the failure of rare earth application be explained in the light of the latest information and knowledge.

Theoretical Analysis and Their Interpretation

In the early 1950's the melting points of the rare earth metals were not exactly known. Since the melting points have been accurately established and are given inTable II along with their transformation temperatures. Only the first six elements of Table II have importance for ferrous-metallurgy at present.

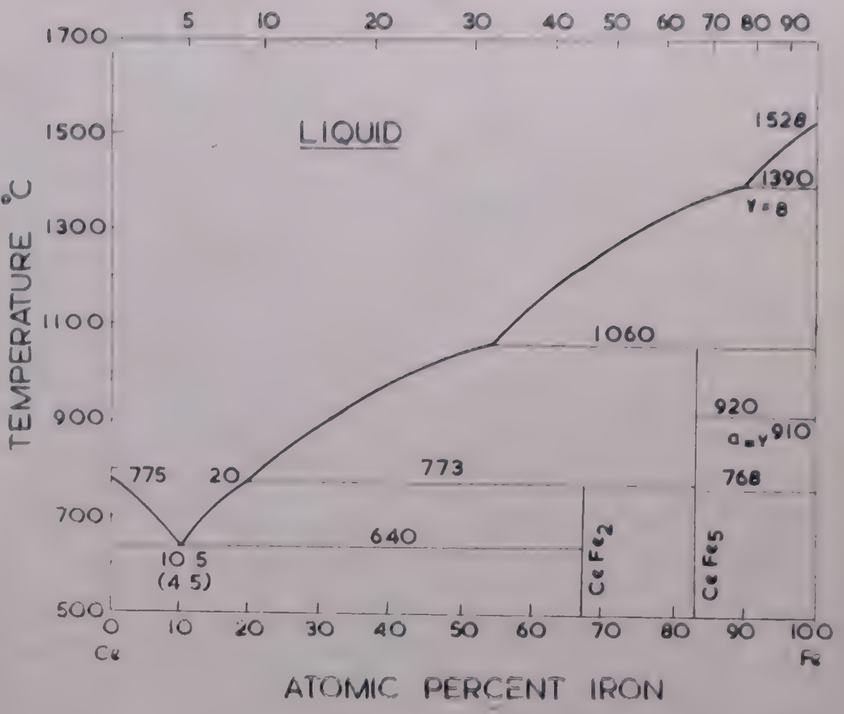
TABLE II **Melting points, transformation temperatures and boiling points of Rare earth metals**

Element		Melting point °C.	Transformation Temperature °C	Boiling Point °C
Scandium	Sc	1 539	1 335	2 727
Yttrium	Y	1 509	1 459	2 927
Lanthanum	La	920	868	3 469
Cerium	Ce	795	725	3 468
Proseodymium	Pr	935	798	3 127
Neodymium	Nd	1 024	862	3 027
Samarium	Sm	1 072	917	1 900
Europium	Eu	826	917	1 439
Gadolinium	Gd	1 312	1 264	3 000
Terbium	Tb	1 356	1 317	2 800
Dysprosium	Dy	1 407	1 317	2 600
Holmium	Ho	1 461	1 317	2 600
Erbium	Er	1 497	1 317	2 900
Tantalum	Tm	1 545	1 317	1 727
Ytterbium	Yb	824	798	1 427
Lutetium	Lu	1 652	798	3 227

Recent studies on magnetic properties of rare earth metals indicated that while gadolinium shows ferromagnetic properties, the more common rare earth metals used in ferrous-metallurgy (Ce, Pr, Ne, etc.) are paramagnetic. It has also been discovered that for corrosion resistance the rare earth metals do not have outstanding properties; as a matter of fact europium is rapidly attacked by moisture at room temperature; lanthanum, cerium and neodymium are also attacked by air, but not as rapidly.

When heated above room temperature, all of the rare earth metals begin to oxidize at relatively low temperature.

From the above two observations one would conclude that rare earth additions would not improve corrosion properties of stainless steels and would also not improve the scale formation of these steels. Their thermal conductivity is low, which again would not permit any change in the heating practices for stainless steels.



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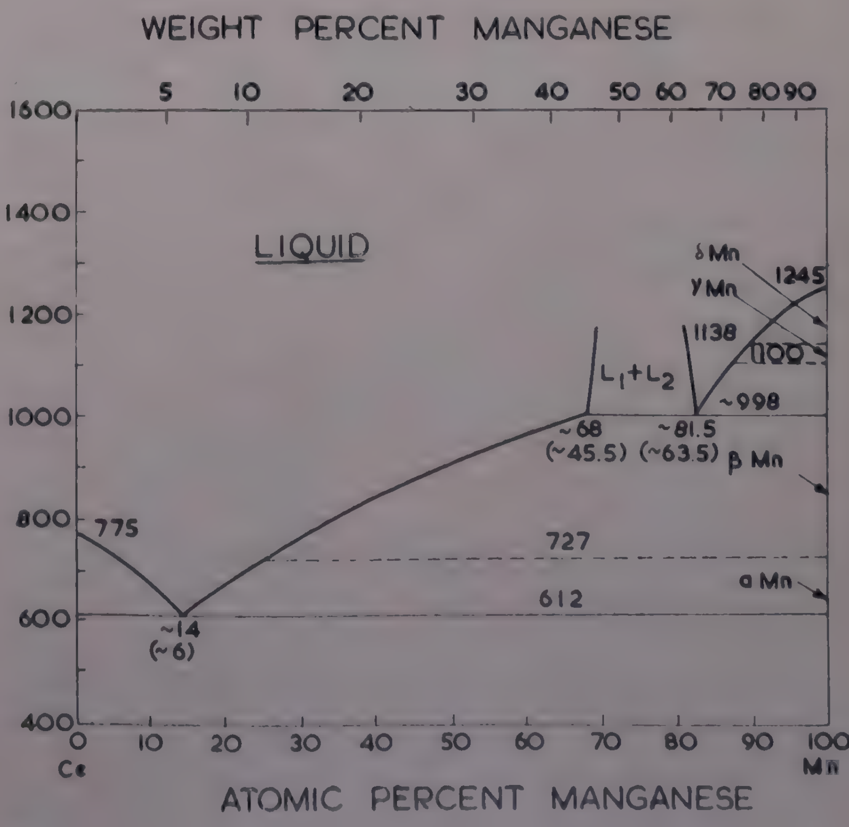
While cerium has a face-centered cubic lattice at room temperature, lanthanum, praseodymium and neodymium have hexagonal structure. It is assumed that the minute addition of rare earth metals to stainless steels would not promote any segregation of these elements, although the solubility of rare earth metals in the multi-component system of stainless steels is not exactly known. The solubility of cerium in iron has been established at 0·4% between 815° and 1015°C.

Being that cerium is the most important rare earth for ferrous application, it seems to be in order to discuss the binary phase diagrams of Ce-Fe, Ce-Mn and Ce-Nif systems as shown by Figs. 1–3.

Fig. 1 Ce-Fe system

Obviously the extreme right side of the diagram is o. interest only for ferrous applications. The cerium lowers the liquidus point of iron very rapidly with increasing concentration, although minute additions such as 2–4 lbs



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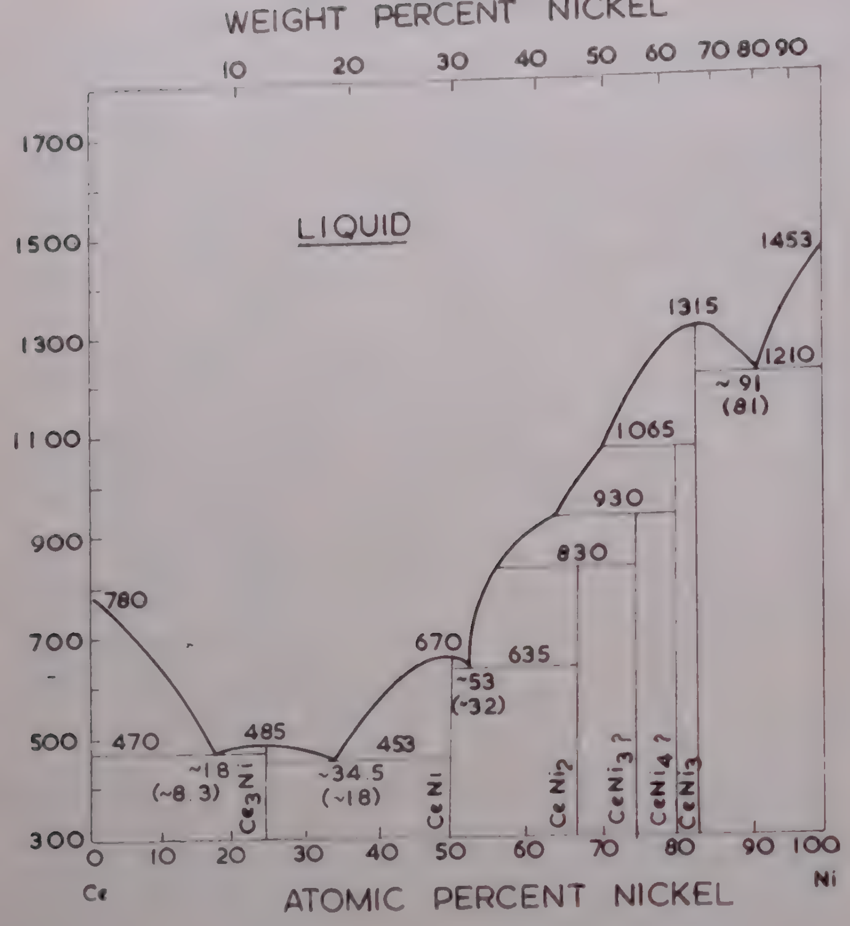


3

per ton of steel will have practically no influence on liquidus point. The claim of increased fluidity of steels by rare earth addition is obviously caused by surface physics rather than by decreased liquidus point.

Two transformations take place in iron-rich Ce-Fe alloys upon heating or cooling. Alpha-Gamma transformation at 920/910°C. and Gamma-Delta transformation at 1390°C. Two intermediate phases are reported-Ce F_2 which forms at 67% Fe (bal. Ce), this phase is face centered cubic, with large lattice parameter, (Å= 7·302 A).Ce F_5 is the other intermediate phase and it forms at 83% Fe (bal. Ce) ; this has à hexagonal structure Å = Angstrome (a = 4·900 Å), c = 4·136 Å).

The formation of these intermediate phases is not very likely with the minute additions of cerium, although by segregation its formation can take place, particularly that of Fe Ce_5.

Fig. 2 Ce-Mn system

Here again the Mn-rich side of the diagram is of interest. This system has no intermediate phases. The liquidus temperature drops sharply with increasing Ce. The first phase transformation upon cooling takes place at 1100°C (delta-gamma), the second at 998°C-(gamma-beta) and the third at 612°C (beta-alpha).

Fig. 3 Ce-Ni system

This system has six intermediate phases, the lowest in cerium is that of Ce Ni_5 at 83% Ni and 17% Ce. This system has no phase transformation.

It is most likely that none of the rare earth metals would form intermediate phase with the more important metallic elements of stainless steels, and one would assume that phase transformations would also not be hindered by the adddition of rare earth metals,

The low melting points of the commercially used are earth metals show they will readily melt aad diffuser within steel at any phase of addition (ladle or mould). Their high boiling points and high heat of vaporization values would indicate that very little sublimation or boiling loss can be expected when alloying rare earth metals, particularly if they are in the form of ferro-alloys. Obviously the relatively low recovery of rare earth addition (50-60%) is assciated with their high rate of oxidation or nitride forming characteristics.

Recent experimental work at ATLAS

Some work has been carried out recently to check up recent claims of Savitskii et al. Fifty ton commercial heats of AISI stainless 316 and 310 have been used with Lan-Cer-Amp addition to 20 lb test ingots poured from the commercial heats prior to tapping. The Lan-Cer-Amp addition was made in the mould ; the standard addition was 0·2% cerium. Parallel test ingots were poured from the heats investigated, one with, the other without Lan-Cer-Amp addition. The test ingots were forged to 1″ square/octagons (reduction 8 : 1). The forged rounds were submitted to chemical analysis to see the effect of rare earth addition.

The results are summarized in Table III.

Table II gives a fair indication that the desulphurizing effect of cerium (and other rare earth present in Lan-Cer-Amp) is practically none. However, a considerable improvement was found in the oxygen content, and the removal of oxygen varied from 25% to 77% ; in any event the reduction in oxygen seems to be significant. This reduction, however, was not verified by inclusion micros, indicating that the oxides have transferred into rare earth oxides which have not been reduced in graphite crucible at 1 850°C.

The forging of test ingots was carried out at 2 075°F and the forgability of test ingots was noted as follows :

Stainless 316	1 345E	without	rare	earth-	good	average
,,	,,	,,	with	,,	,,	,,	,,
,,	,,	1 346E	without	,,	,,	,,	,,
,,	,,	,,	with	,,	,,	,,	,,

As it can be seen from the above, if the heat was made under proper melting conditions the rare earth additon shows no drastic improvement.

Annealing test was carried out to study the progress of transformation and temperatures have been selected between 1 600°F and 2 000°F. Photoseries show the structures obtained at various annealing temperatures. Specimens were annealed in electric resistance furnaces, heated up for the specified temperatures in 15 minutes and held at the annealing temperatures for 15 minutes, then water-annealed. Micros were examined at 500 magnification after electrolytical etching in oxalic acid. The interpretation of micro-photos is given in the following :

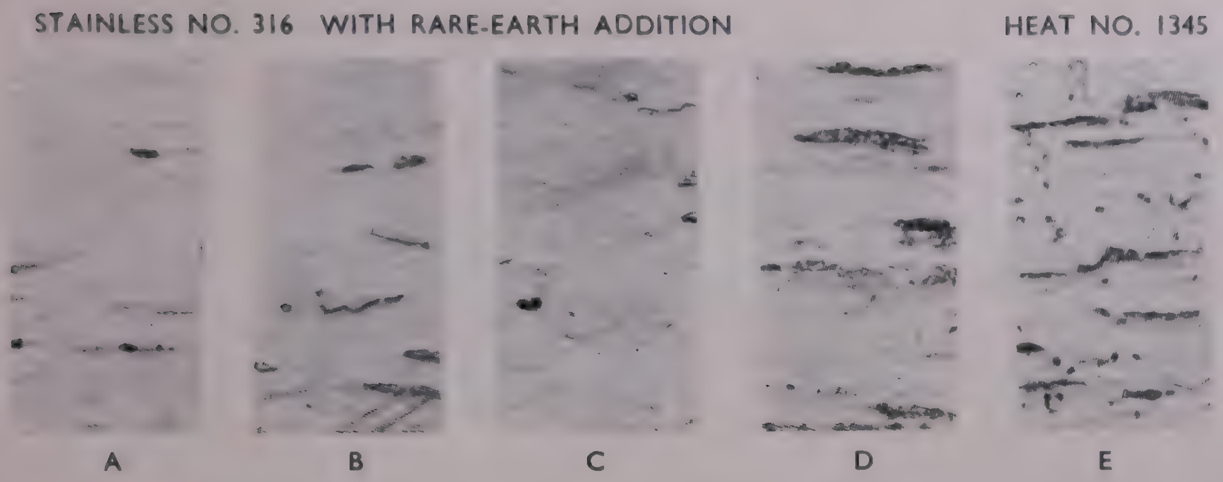
Photoseries No. 1—No rare earth addition

AISI Stainless 316—Heat No. 1345 E.

(*a*) As forged sample. Approximately 5% ferrite. Note dark constituents in the ferrite-field.

(*b*) Annealed at 2000°F. Approximately 5% ferrite still present but dark constituent disappeared, obviously went into solution.

(*c*) Annealed at 1900°F. This annealing temperature is not enough to take all dark constituents into solution.



P. 1 *All specimens were electrolitically etched for 1 min in 10% oxalic acid.* ×500

TABLE III Chemical analysis of 316 and 310 austenitic stainless steels—with and without rare earth additions

Type	Heat No.	Analysis Sample Location	C	Mn	S	Cr	Ni	O_2	Rare earth Addition
316	1 345 E	Bottom	0·07	1·79	·019	17·89	11·42	·0109	None
316	1 345 E	Top	—		·020			·0205	,,
316	1 345 E	Bottom			·019			·0083	0·2 Ce
316	1 345 E	Top	·055	1·84	·019			·0048	0·2 Ce
316	1 346 E	Bottom	·055	1·84	·016	17·18	10·51	·0081	None
316	1 346 E	Top			·016			·0089	,,
316	1 346 E	Bottom			·016			·0038	0·2 Ce
316	1 346 E	Top			·016			·0016	0·2 Ce
310	B 7 246	Bottom	·115	2·02	·016	25·81	18·80	0·0133	None
310	B 7 246	Top			·015			·0230	,,
310	B 7 246	Bottom			·016			·0070	0·2 Ce
310	B 7 246	Top			·017			·0060	0·2 Ce

(*d*) Annealed at 1800°F. Increasing ferrite lines with dark constituent.

(*e*) Annealed at 1600°F. Approximately same amount of ferrite with increasing dark constituents, scattered all over. This dark constituent is iron-chromium-carbide.

Photoseries No. 2—0·2% Ce addition

AISI Stainless 316—Heat No. 1345 E.

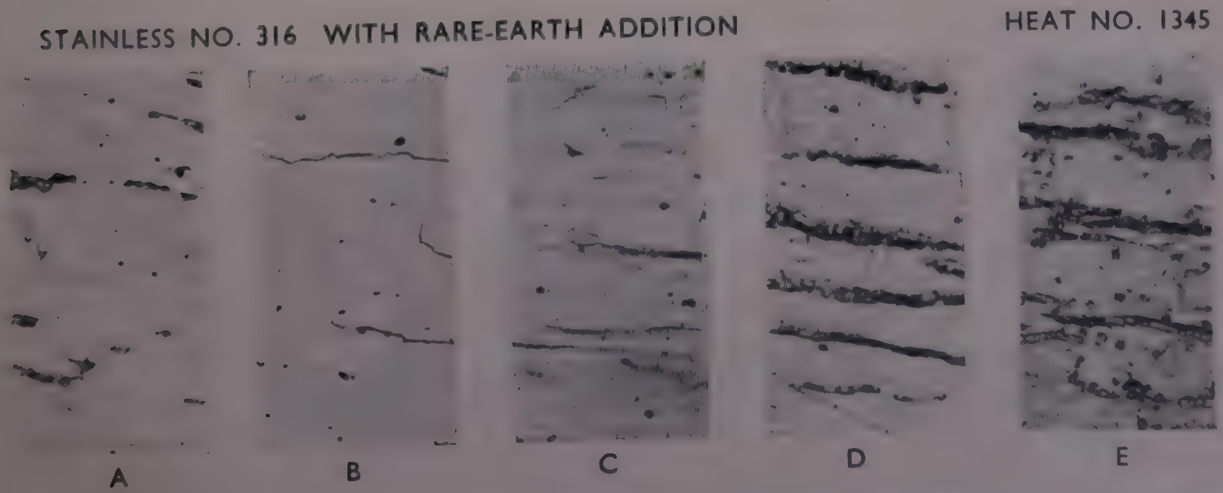
Shows identical samples from the test ingot alloyed with 0·20 cerium. There is no reduction in the amount of ferrite, as a matter of fact there is rather a slight increase. The noticeable difference, however, is the heavier segregation of carbides, indicating that rare earth alloyed stainless 316 cannot retain the carbides in solution as readily as the austenite-ferrite matrix without rare earth alloy addition. This seems to be the case for all temperatures investigated.

Photoseries No. 3—No rare earth addition

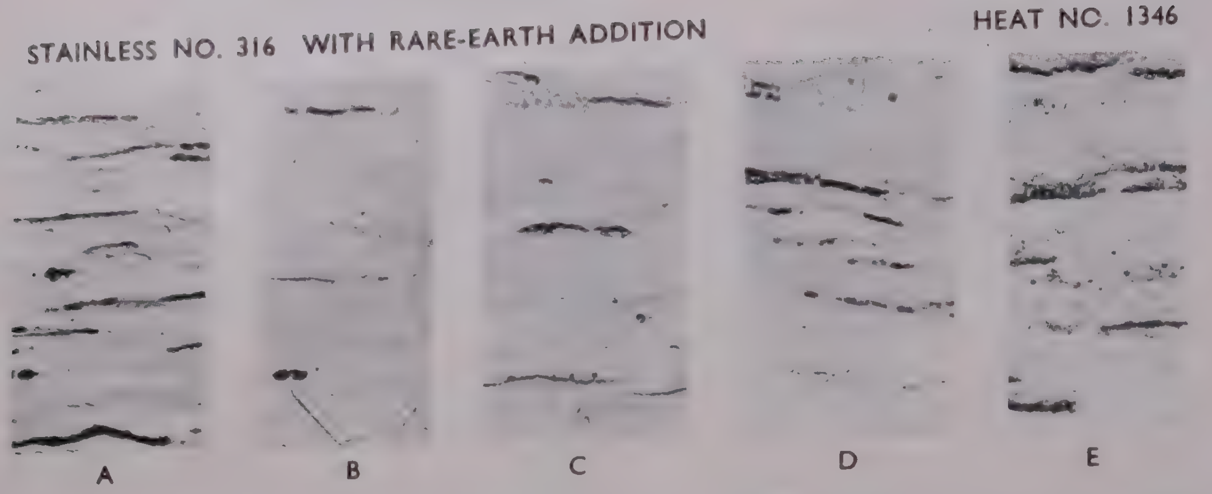
AISI Stainless 316—Heat No. 1346 E.

(*a*) As forged sample. The amount of ferrite is slightly higher than in sample 1-a., with considerably more precipitated carbide present.

(*b*) The ferrite almost completely disappeared, with approximately 1–2% present after 2000°F. anneal.



P. 2 *All specimens were electrolitically etched for 1 min in 10% oxalic acid.* ×500


STAINLESS NO. 316 WITH RARE-EARTH ADDITION
HEAT NO. 1346
A
B
C
D
E

P. 3 *All specimens were electrolytically etched for 1 min in 10% oxalic acid.* ×500

(*c*) Approximately 2-3% ferrite present after 1 900°F annealing, with some precipitated carbides.

(*d*) Slightly increased ferrite but considerably increased precipitated carbide is present in the sample annealed at 1 800°F.

(*e*) Approximately 6-7% ferrite with primarily ferrite based, plus some scattered precipitated carbides.

Photoseries No. 4—0·2 Ce alloyed

AISI stainless 316—Heat No. 1346 E.

There is no improvement in the percentge of ferrite; on the contrary even the sample annealed at 2 000°F shows 1-2% ferrite and some carbides. Generally speaking, all corresponding samples are somewhat worse than the samples of the same heat without rare earth addition.

Photoseries No. 5—Without rare earth addition

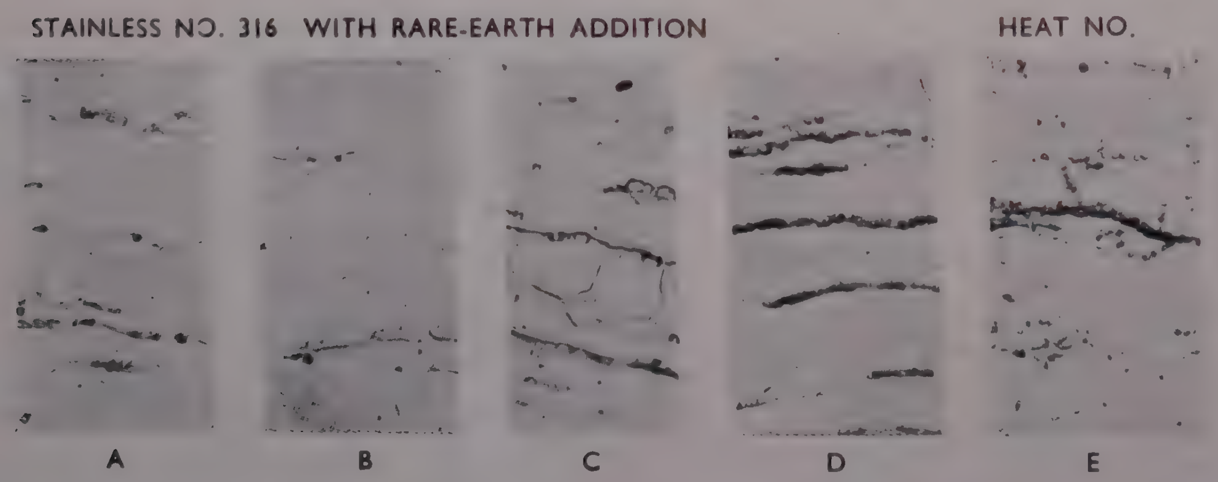
AISI Stainless 310

(*a*) The microphoto of as-forged sample shows relatively coarse grains, some carbide-precipitation, and pratcially no ferrite in the structure.

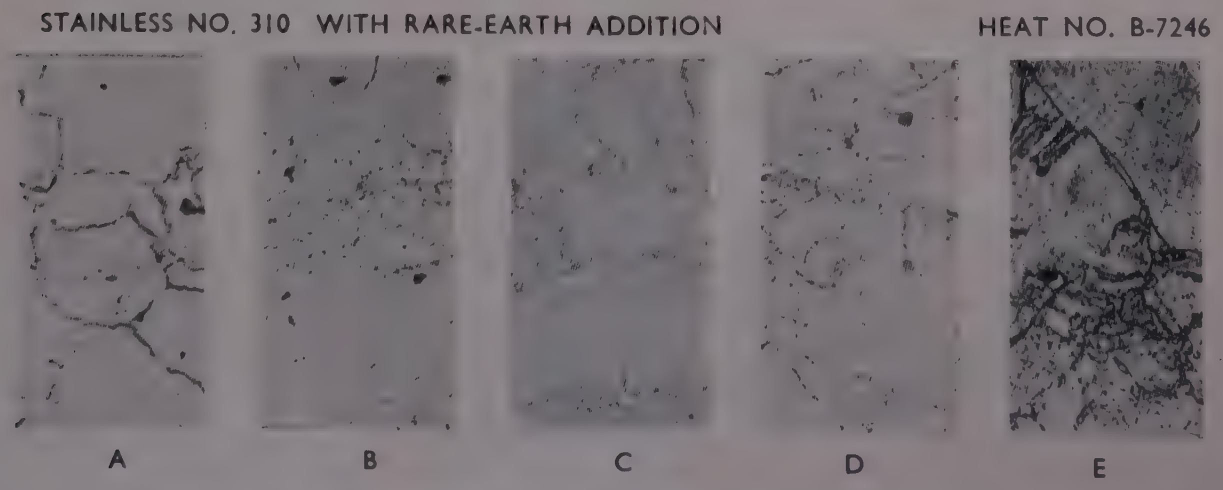
(*b*) The proper annealing at 2000°F eliminated all grain-boundary precipitates but the intragranular precipitation is still present.

(*c*) Annealing the sample at 1900°F some ferrite became visible, approximately 2-3%, with an increasing amount of precipitated carbide.

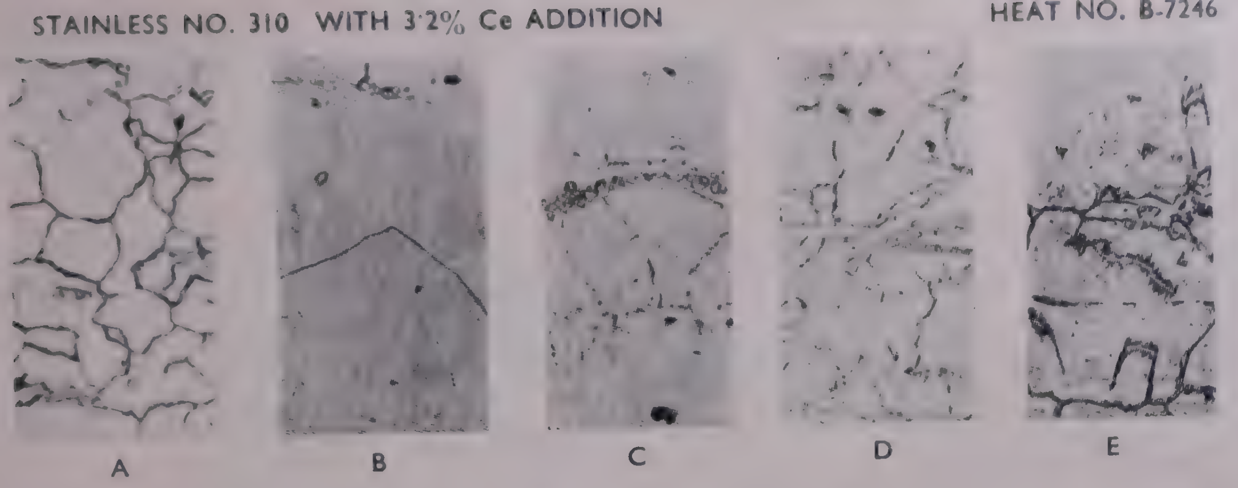
(*d*) Annealing at 1800°F. introduced grain-boundary


STAINLESS NO. 316 WITH RARE-EARTH ADDITION
HEAT NO.
A
B
C
D
E

P. 4 *All specimens were etched electrolitically for 1 min in 10% oxalic acid.* ×500


STAINLESS NO. 310 WITH RARE-EARTH ADDITION
HEAT NO. B-7246
A
B
C
D
E

P. 5 *All specimens were electrolitically etched for 1 min in 10% oxolic acid.* ×500



P. 6 *All specimens were electrolitically etched for 1 min in 10% oxalic acid.* %500

precipitates with the same amount of ferrite.

(*e*) Annealing the sample at 1600°F. shows abundant carbides which the austenite was not capable of dissolving at this low temperature, and ferrite was developing along the grain boundaries. In this sample some sigma phase is also present.

Photoseries No. 6—With 0·2% Ce addition

AISI Stainless 310

(*a*) The as-forged sample is identical to the sample without rare earth addition. The percentage of ferrite present is perhaps slightly more.

(*b*) The sample annealed at 2000°F. shows slightly less precipitated carbides than its counterpart.

(*c*) Sample annealed at 1900°F. shows considerably less precipitated carbides than its counterpart.

(*d*) Annealing at 1800°F. produced just as much grain boundary precipitation as the sample without cerium addition.

(*e*) Annealing the sample in the sensitizing zone (1600°F) not only produced a considerable amount of intragranular carbide precipitation but a significant percentage of ferrite is also present in the sample.

Comparing the samples of rare earth alloyed and unalloyed test ingots, one can easily conclude that the addition of 0·2% cerium produced no effect in eliminating the formation of ferrite or in reducing carbide precipitation. Since this is the rare earth percentage recommended by most authors, the merit of such rare earth addition is rather questionable.

A comparison of mechanical properties is also of interest in considering the overall merit of rare earth addition to stainless steels. Tensile strength, yield strength, elongation, reduction of area and brinell hardness values were measured on all samples and the results obtained are summarized in Tables IV and VIII. The comparison clearly illustrates that there is only a minor difference between the properties of steels with and without 0·2% cerium addition.

TABLE IV **Tensile properties of AISI stainless 3.6 steels with and without rare earth addition**

Tensile strength Lb per sq in Annealing Temperature F.	Heat 1345 E No. R. E.	Heat 1345 E 0·2 Cerium	Heat 1386 E No. R. E.	Heat 1386 E 0·2 Cerium
2 000	83 500	81 000	83 750	83 000
1 900	84 000	84 000	84 000	83 500
1 800	89 500	86 500	85 500	85 500
1 600	86 500	86 500	88 500	88 500

TABLE V **Yield strenth properties of AISI st. 316 steels with and without rare earth addition**

Yield Strength lb per sq in Annealing Temperature °F	Heat 1345 E No. R. E.	Heat 1345 E 0·2% Cerium	Heat 1396 E No. R. E.	Heat 1396 E 0·2% Cerium
2 000	40,000	37,500	43,000	39,500
1 900	39,000	41,000	38,250	39,000
1 800	39,500	42,000	41,000	40,500
1 600	47,500	46,000	42,000	42,000

TABLE VI **Elongation of AISI stainless 313 steels with and without rare earth addition**

Elongation, % Annealing Temperature °F	Heat 1345 E No. R. E.	Heat 1345 E 0·2% Cerium	Heat 1345 E No. R. E.	Heat 1345 E 0·2% Cerium
2 000	55	59	57·5	58
1 900	54	55	58	53·5
1 800	50·5	50·5	50	51
1 600	40	32	46	50

TABLE VII **Reduction of area of AISI stainless 316 steels with and without rare earth addition**

Reduction of area, % Annealing Temperature °F	Heat 1345 E No. R. E.	Heat 1345 E 0·2% Cerium	Heat 1346 E No. R. E.	Heat 1346 E 0·2% Cerium
2 000	71·7	71·7	69·4	74·9
1 900	71·4	71·4	70·1	71·7
1 800	70·3	64	67·7	70·3
1 600	52·6	43·9	60·6	65·0

TABLE VIII **Brinell-Hardness values of AISI stainless 316 steels with and without rare earth addition**

Annealing Temperature °F	Heat 1345 E No. R. E.	Heat 1345 E 0·2% Cerium	Heat 1346 F No. R. E.	Heat 1346 F 0·2% Cerium
2 000	146	143	137	137
1 900	149	149	143	148
1 800	149	152	149	149
1 600	149	167	149	156

TABLE IX Magnetic permeability of AISI stainless 316 steels with and without rare earth addition

Annealing Temperature °F	Heat 1345 E		Heat 1346 E	
	No R. E.	0·2% Cerium	No R. E.	0·2% Cerium
As Forged	1·15	1·15	1·10–1·15	1·10–2·15
2 000	1·10--1·15	1·10–1·15	1·02–1·05	1·02–1·05
1 900	1·10–1·15	1·15	1·05–1·10	1·02–1·05
1 800	1·10–1·15	1·05–1·10	1·05–1·10	1·05–1·10
1 600	1·02–1·05	1·02–1·05	1·10–1·15	1·10–1·15

The magnetic permeability of each specimen was also performed on stainless 316 heats and the results are given in Table IX.

While there is considerable variation between magnetic permeability of each specimen, the rare earth treated samples showed no improvement.

Summary

The recent experiments on AISI stainless 316 and 310 steels confirmed the former results of North American experiments. The use of rare earth metals cannot be justified for stainless steels since there is no consistency in the improvement of any properties. The claimed higher austenitic stability cannot be achieved simply by adding rare earth metals – the austenitic stability depends on many other factors which can be controlled by other means during steel-making.

It became obvious that the addition of 0·2% cerium to the above grades :

1. Did not improve hot-workability.
2. Did not improve carbide-segregation and sensitization characteristic of the steels involved.
3. Did not improve mechanical properties.
4. Did not improve magnetic permeability of steels.
5. Did not improve austenitic stability.
6. Did not improve sulphur removal.

The only improvement was that in oxygen-removals as indicated by oxygen analysis; cleanliness micros, however, did not verify this improvement.

Unfortunately, steelmakers and metallurgists will have to find other means of improving the above properties. Rare earth additions do not seem to be able to solve the numerous problems of austenitic stainless steel processing.

Acknowledgement

The author is very grateful to the Management of Atlas Steels Company, Welland, Ontario, Canada for permitting the presentation of this paper.

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On the Transformation of Austentite to Martensite and the Tempering Process of Martensite in Iron-Nitrogen System

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M. Izumiyama
M. Tsuchiya

THE transformation of austenite to martensite and the tempering of martensite in iron-carbon system have been investigated by several workers but very few studies[1-5] have related to the problem in iron-nitrogen system, in spite of the fact that both nitrogen and carbon have similar atomic volumes and that a forced interstitial solid solution is formed in iron.

In the present work the authors have studied the transformation of austenite to martensite based on statistical thermodynamics and crystallography using Fe-N alloys, and have compared the results to those obtained with Fe-C alloys. Studies on tempering of martensite and austenite in Fe-N alloys were carried out by X-ray diffraction analysis.

Excess free energy must be stored to resist the considerable strain produced by transformation of austenite to martensite. Therefore, the transformation to martensite will not proceed at To temperature at which $-\Delta F^{\gamma\rightarrow\alpha'} = O$, i,e., at the metastable equilibrium temperature between austenite and martensite, the austenite being supercooled to the Ms point at which the martensite begins to form. The strored free energy caused by this superecooling will probably play the the role of the driving force necessary for initiating the transformation of austenite to martensite and as such a thermodynamic study on the transformation of austenite to martensite would provide useful information on the range of supercooling from To to Ms point. and the amount of free energy that will be stored by this supercooling.

The martensite plate is formed by geometrical deformation. It has been observed that habit plane of the martensite plate in Fe-C alloy containing about 1.7 weight % C is (259γ[6]. It would be interesting to determine the Miller index for the habit plane of an Fe-N alloy.

Experiments

The specimens used were prepared from pure iron by nitriding with a gas mixture of ammonia and hydrogen. The compositions of pure iron are shown in Table 1. Specimen No. 1 is commercial pure iron powder of about 55 mesh and specimen No. 2 is pure iron plate 0.15 mm thick. Specimen No. 2 was made from a 1·2 kg ingot which was melted in vacuum by a high frequency induction furance. After casting in a chill mould 30 mm diameter, the ingot was hot-worked and cold-rolled into a plate of 0.15 mm thickness. The plate was then annealed at 1000°C for 1 hour in vacuum, and cut into a piece 50 mm long, 10 mm wide and 0.15 mm thick.

TABLE I Chemical compositions of specimens used, (wt %)

Specimen	C	Si	Mn	P	S	N
Pure Iron Power	0·004	0·021	0·039	0·006	Trace	0·008
Pure Iron Plate	0·003	0·008	0·002	0·004	0·005	0·002

Nitriding was carried out for 5 hours at 650°C which is the temperature of maximum solubility of nitrogen in austenite; nitrogen content in iron was controlled varying the amount of hydrogen and the specimens were quenched in water.

Ms point was determined microscopically with specimen No. 2 by the Greninger and Troiano method[7] i.e. by studying the microstructure in which martensite plates are formed uniformly in austenite, showing that the concentration of nitrogen in austenite is almost homogeneous. The amount of nitrogen absorbed was determined by Kjeldahl method and also by weight decrease measurement after heating; in the latter method after nitriding, the layer of nitride (0·02–0·03 mm) on the surface, was removed electrolytically, in a solution of 200 cc. of phosphoric acid and 100 gm of chromic acid with a current density of 2-3 amp./dm², using 18-8 stainless steel cathode; the specimen was weighed and then heated to 1 000°C for 12 hours, and subsequently to 700°C for 6 hours in a vacuum furnace to eliminate its nitrogen; the specimen was again weighed and the amount of nitrogen was determined as the difference between the two weights.

Figure 1 shows a comparison of the two methods; in this work nitrogen was determined mainly by the weight

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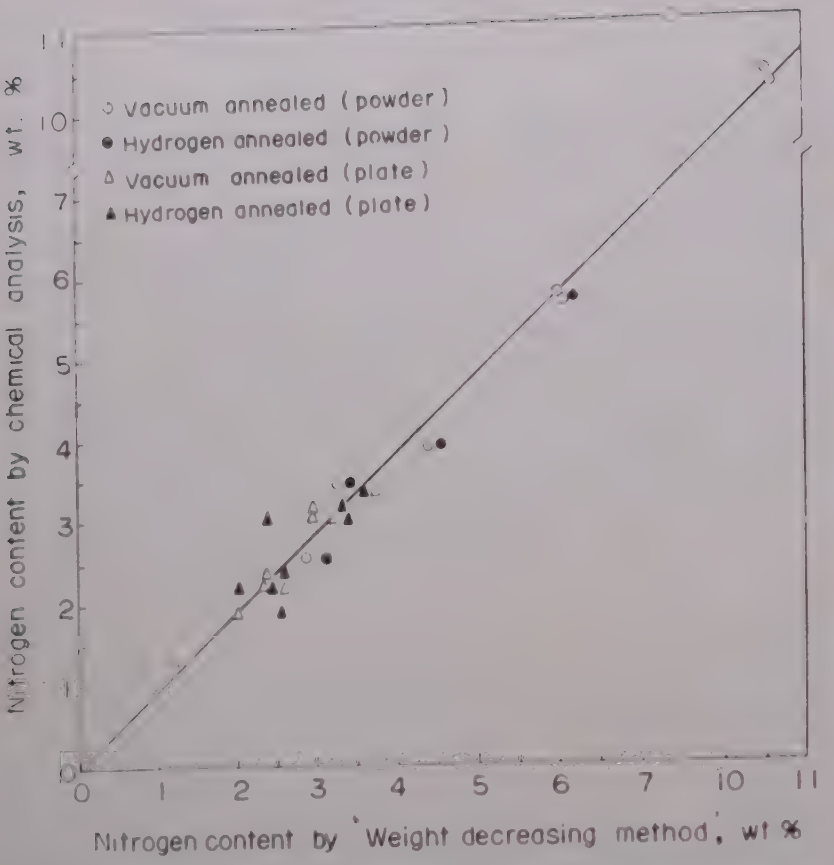


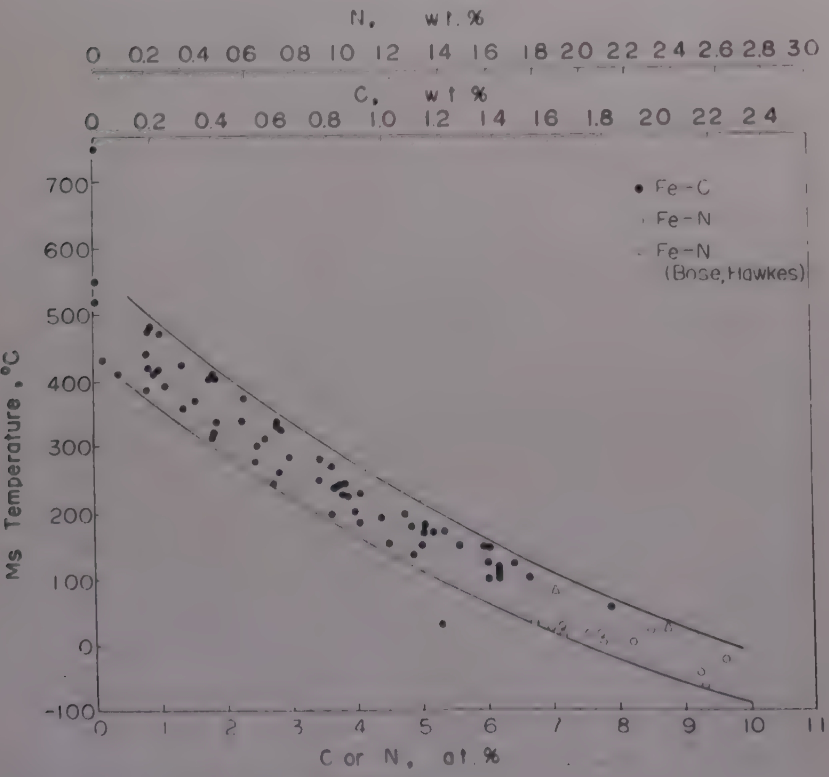
1 *Comparison of nitrogen contents in Fe-N alloys, determined by weight decrease measurement and by Kjeldahl method.*

decrease measurement and corrected by the straight line shown in Fig. 1.

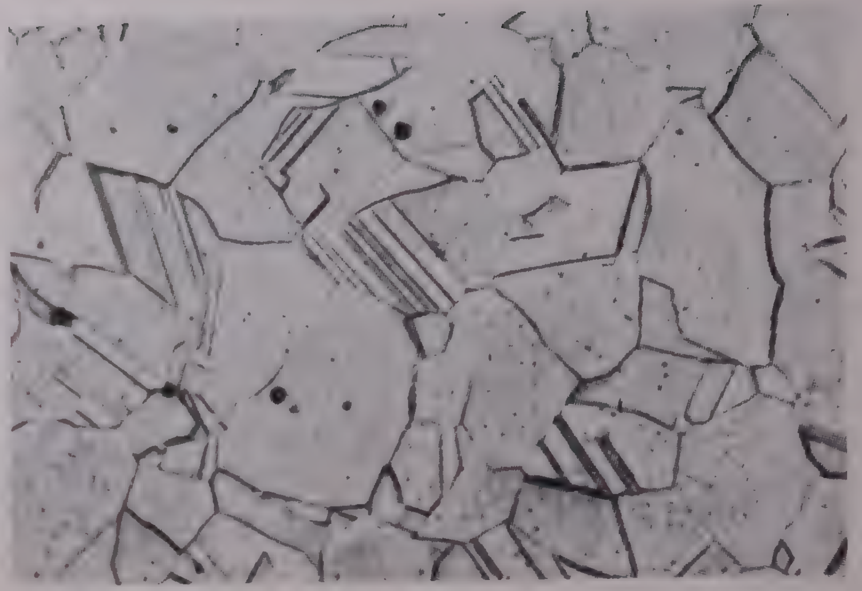
The lattice parameters of austenite and martensite were measured by X-ray diffractometer using iron target and manganese filter.

Results

Fig. 2 shows the Ms points obtained in the present work for high nitrogen Fe-N alloys and those of Fe-C alloys reported by previous works. In Fe-N alloys the two points by Bose and Hawkes[3] are the only data which have been reported previously. As shown in this figure, the relation between Ms point and nitrogen content in Fe-N alloys and carbon content in Fe-C alloys is in good agreement, the Ms point descending to room temperature at about 2·2 weight %N. Therefore, in alloys containing higher nitrogen a complete austenitic structure is obtained at room temperature.



2 *Ms points in Fe-C and Fe-N alloys.*



3 *Austenite in iron-nitrogen alloy (2·39 wt % N).* ×700

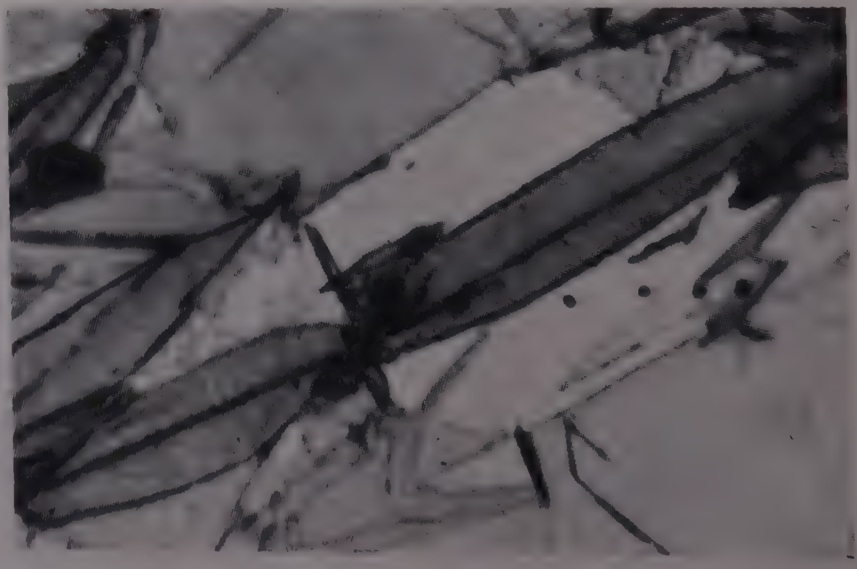
Figure 3 shows a micro-structure of austenite in the Fe-N alloys, and Fig. 4 a micro-structure of austenite and martensite. The martensite in this alloy appears in a lenticular form having a mid-rib as that in iron-carbon alloy.

Figures 5 and 6 show the lattice parameters of austenite and martenite in Fe-N and Fe-C alloys, including results of other workers.[3–5, 8–10] It may be observed from this figure that the lattice parameters of austenite and martensite in Fe-N alloys coincide with those in Fe-C alloys respectively.

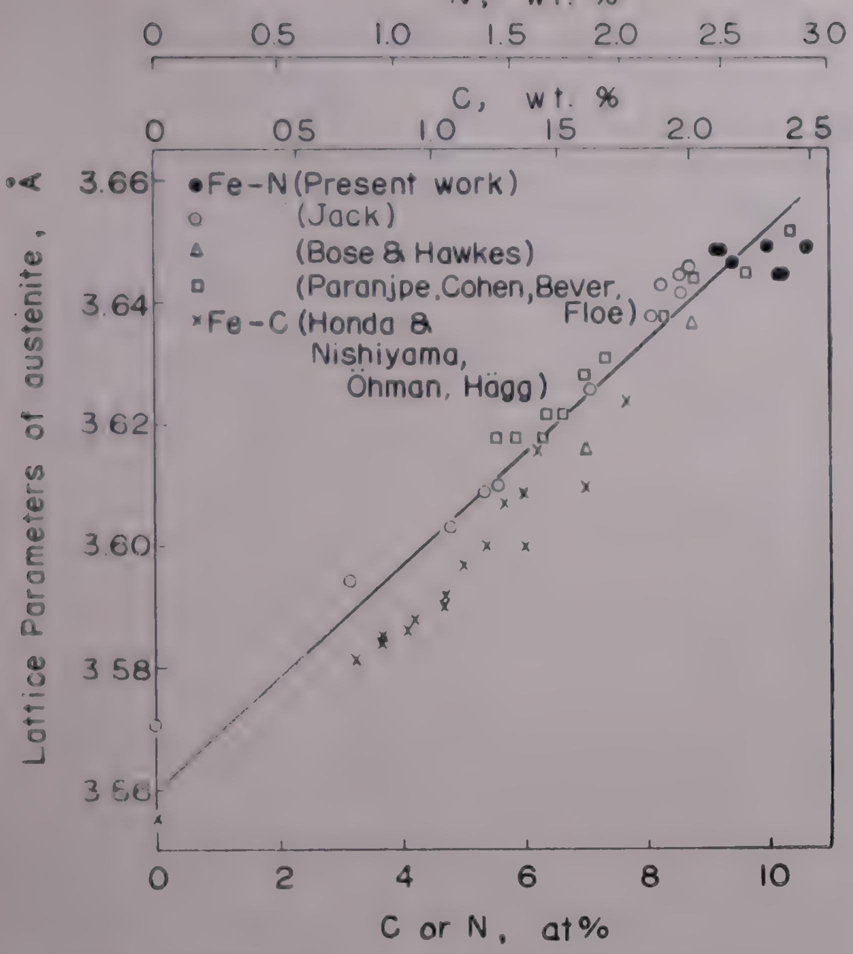
Generally, from the crystallographic point of view, the transformation of austenite to martensite in the interstitial solid solution being a transition of face centered cubic to body centered tetragonal structure, the difference between the chemical free energy of austenite and martensite $(-\Delta F^{\gamma\rightarrow\alpha'})$ can be expressed as follows:

$$-\Delta F^{\gamma\rightarrow\alpha'} = -\Delta F^{\gamma\rightarrow\alpha} - (-\Delta F^{\alpha\rightarrow\alpha'}) \quad \ldots \quad (1)$$

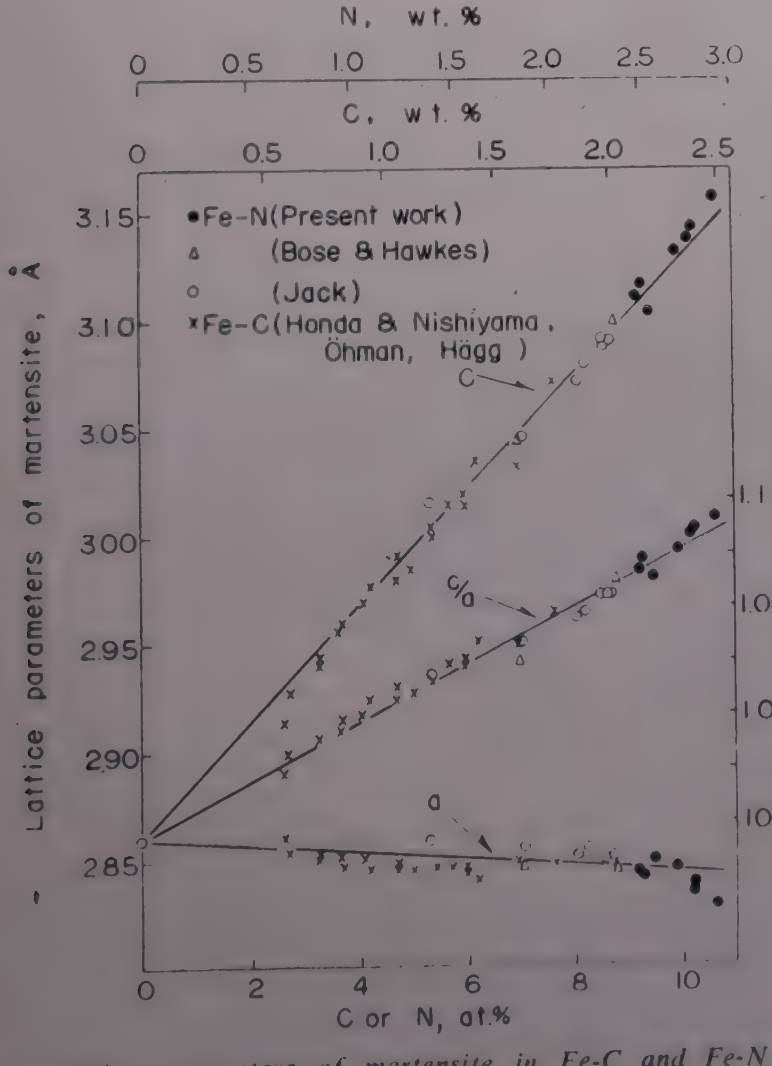
where α denotes body centered cubic iron with solute



4 *Marensite in iron-nitrogen alloy (2·07 wt % N).* ×2 200



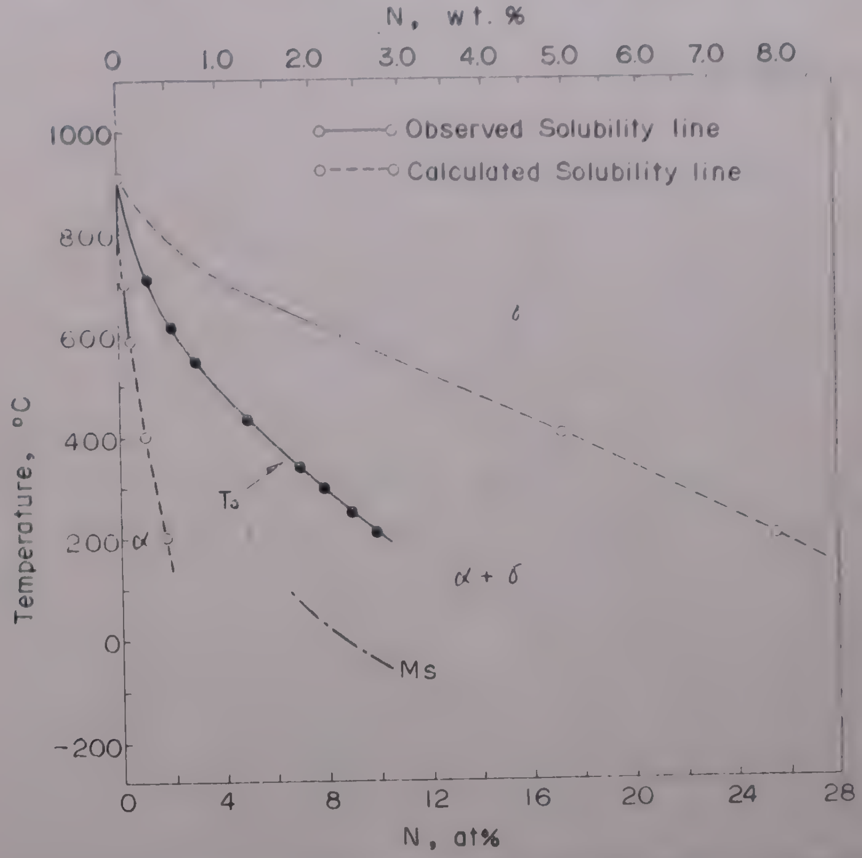
5 *Lattice parameters of austenite in Fe-C and Fe-N alloys.*



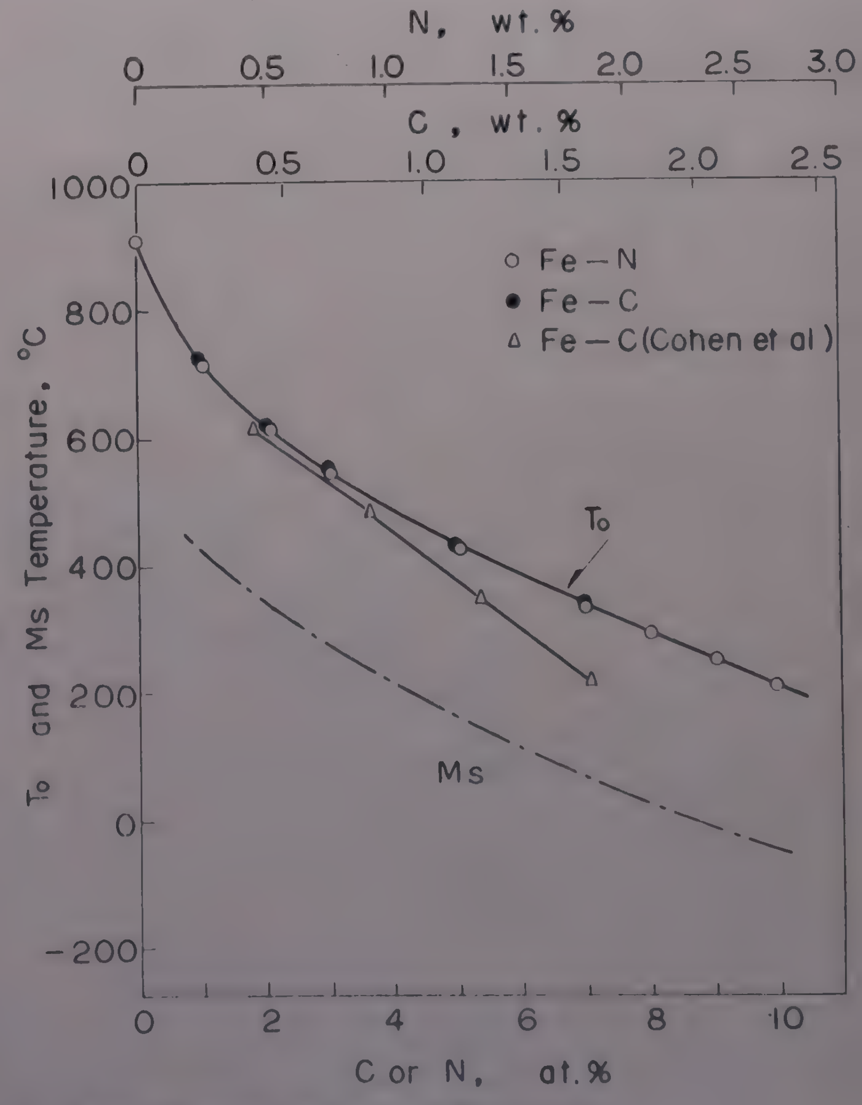
6 *Lattice parameters of martensite in Fe-C and Fe-N alloys. Axial ratio also shown.*

atoms dissolved in random interstitial positions and with the same amount of solute atoms as in the original austenite phase. The stepwise process indicated by equation (1) is only for calculation purposes. Tσ shows the temperature at which $-\Delta^{\gamma\to\alpha'}=0$ in equation (1).

Figure 7 shows metastable mutual solubility curves of α and γ phases, Tσ-points derived from equation (1) and Ms-points in Fe-N alloys. As shown in this



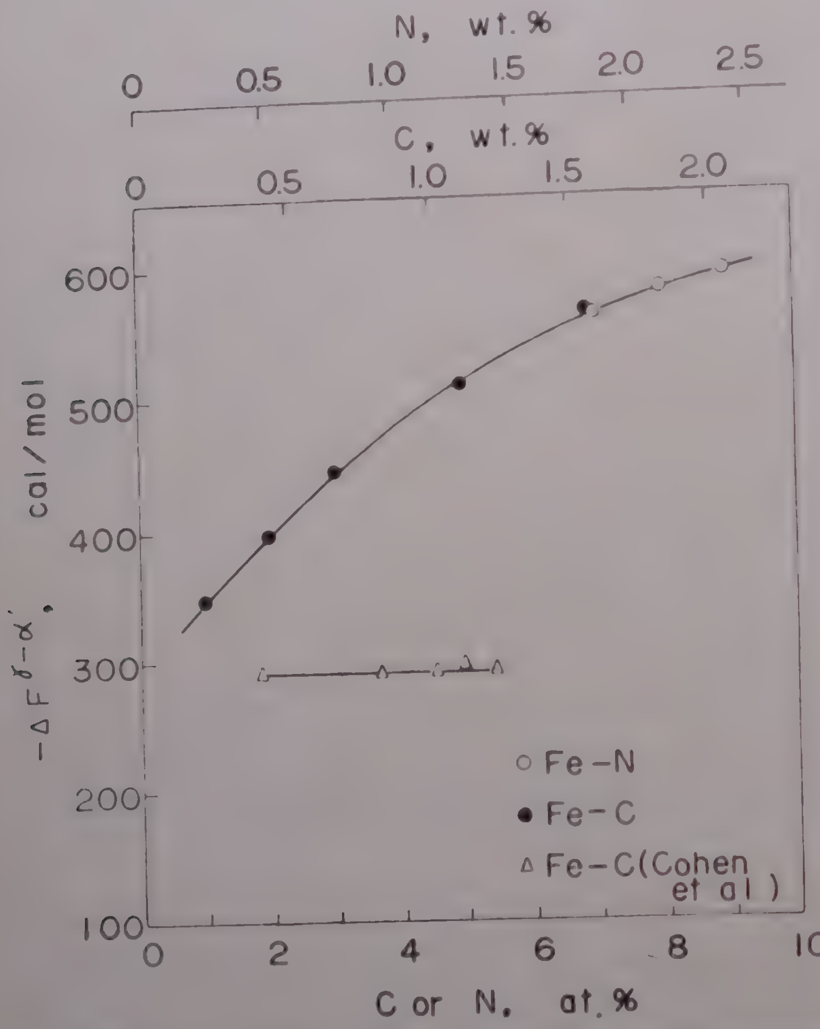
7 *Metastable mutual solubility curves of α- and γ-phases. To and Ms points in Fe-N alloys.*



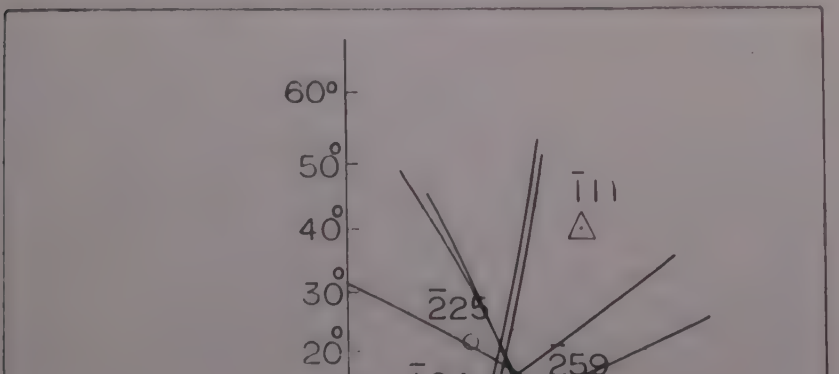
8 *To and Ms points in Fe-N and Fe-C alloys.*

figure, the transformation of austenite to martensite will not occur prior to supercooling at about 280°C.

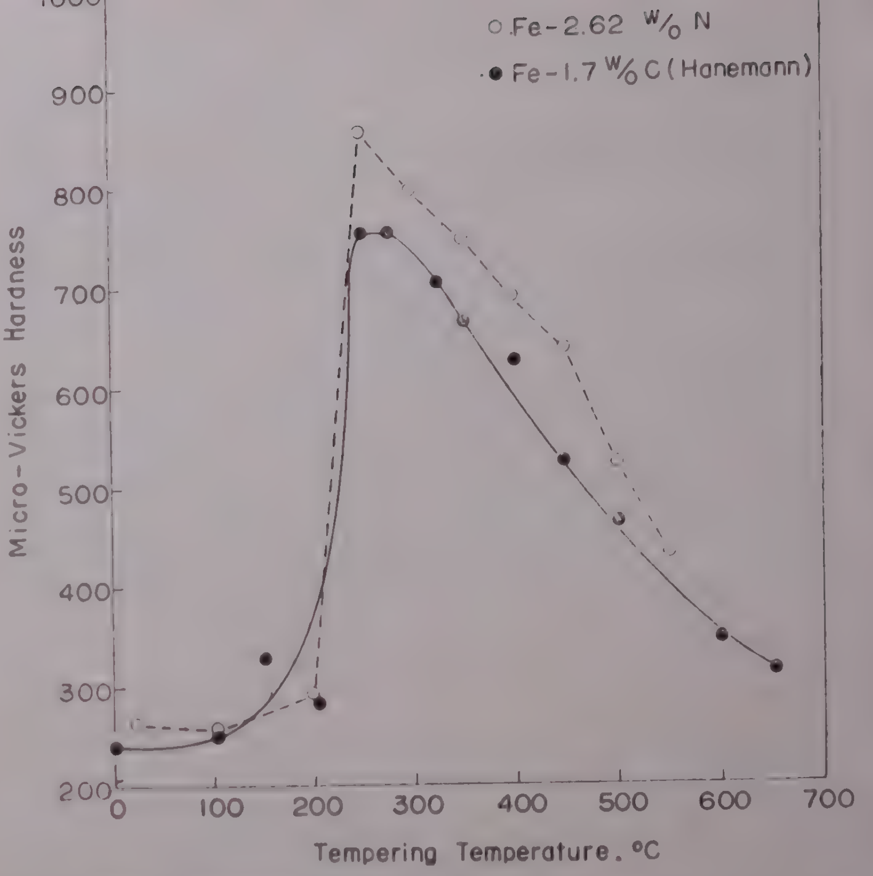
Figure 8 shows Tσ and Ms points in Fe-N and Fe-C alloys, in which we can see that the Tσ temperatures in both alloys are nearly equal. The Tσ temperatures in iron-carbon alloys calculated by the previous workers[11] coincide with the results obtained in the present work up to about 3 atomic %C, beyond which they deviate.



9 *Comparison of driving of proces to initiate martensite formations in Fe-C and Fe-N alloys.*



10 *Habit plane of martensite in Fe-N alloy containing 2·0 wt % N shown by stereographic projection.*



11 *Change of hardness due to tempering of austenite in Fe-F and Fe-C alloys.*

Figure 9 shows the driving forces ($-\triangle F^{\gamma\to\alpha'}$) necessary for the formation of martensite in Fe-N and Fe-C alloys at Ms points. The driving forces in both alloys are nearly equal and increase as the content of solute atoms increases.

From the above results, it is concluded that the thermodynamic properties of Fe-N and Fe-C alloys are quite similar.

Figure 10 shows the habit plane of martensite in Fe-N alloys containing 2·0 weight %N obtained by stereographic projection. This figure was obtained by one surface analysis using slip planes or twin boundaries with four (111)γ traces. As shown in this figure the large circles including the habit plane intersect around (259)γ. This habit plane coincides with that of Fe-C alloy containing more than 1·7 weight %C.

Figure 11 shows the change of hardness due to tempering at various temperatures for 1 hour, using austenitic steels obtained by quenching of the Fe-C alloys.[12] The hardness of these alloys increase remarkably at about 200°C and reaches a maximum at about 250°C on tempering.

Table II shows the result of X-ray diffraction analysis of Fe-N alloy with 2·2 weight %N consisting of austenite and martensite, tempered at various temperatures for 1 hour.

$Fe_{16}N_2$ (α″) revealed itself on tempering at 150°C, and $Fe_{16}N_2$ (α″) and Fe_4N (γ)′, at 2000 C. When tempering temperature rises above 250°C only Fe_4N was observed. On tempering of alloy wholly consisting of austenite, no precipitate was observed up to 200°C, being decomposed to ferrite and Fe_4N(γ′) above this temperature as shown in Table III.

From these Tables, it is seen that martensite first precipitates $Fe_{16}N_2$ (α″) and changes into Fe_4N (γ′), Fe_4N being directly separated from austenite. It is noticeable that no F_3N(ε) phase is detected on tempering of Fe-N alloys with more than 2 weight %N, consisting of martensite or austenite.

TABLE II Results of diffraction analysi of Fe-N alloy with 2·2 wt % N, tempere1. Quenched structure consists of martensite and austenite.

No	150°c x 1h		200°c x 1h		250°c x 1h		300°c x 1h		500°c x 1h		α''-$Fe_{16}N_2$ [13]		γ'-Fe_4N [14]	
	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I/I_1	d (Å)	I/I_1
1			2.190	vs	2.190	vs	2.190	vs	2.190	vs			2.191	100
2	2 115	vs	2.112	vs							2.114	100		
3	2.019	m	2.021	m							2.019	57		
4			1 909	s	1.899	m	1.899	m	1.896	m			1.897	77
5			1 576	vvw							1.573	11		
6	1 430	m	1 432	w							1.428	28		
7			1.337	w	1.341	m	1.344	s	1.341	m			1.342	67
8	1 241	w	1.244	w							1.241	28		
9	1 180	s	1.184	m							1.183	86		
10					1.149	w	1.147	w	1.145	w			1.144	83
11			1 015	vw							1.015	67		

TABLE III Result of diffraction fnalysis of Fe-N alloy with 2·43 wt % N, tempered. Quenched structure consists of austenite

No	250°c x 1h		300°c x 1h		500°c x 1h		γ'-Fe_4N [14]	
	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I/I_1
1	2.189	VS	2.196	VS	2.193	VS	2.191	100
2	1.901	m	1.899	m	1.900	m	1.899	77
3	1.344	m	1.342	s	1.344	s	1.342	67
4	1.147	w	1.144	m	1.145	m	1.144	89

To sum up the results obtained in the present study:

1. Ms points in Fe-N and Fe-C alloys containing equal amount of solute atom show good agreement. Ms point in Fe-N alloys gradually drops as N content increases, and it reaches room temperature for about 2·2 weight %N. Hence, in higher N alloys whole austenitic structure can be obtained at room temperature.
2. The martensite plate in Fe-N alloys with high nitrogen is of lenticular form having a mid-rib, as that in Fe-C alloys. The habit plane of martensite in high nitrogen alloys is $(259)\gamma$ and coincides with that of Fe-C alloys containing more C than 1·7 weight %.

   $T\sigma$ point-composition curves in Fe-N and in Fe-C alloys show good agreement and the transformation of austenite will not occur prior to super-cooling at about 280°C.
4. The driving forces necessary to transform austenite to martensite in Fe-N and in Fe-C alloys at Ms point also show good coincidence and the driving forces increase as the content of solute atom increases.
5. On tempering, nitride $Fe_{16}N_2(\alpha'')$ which changes into $Fe_4N(\gamma')$ precipitates from martensite and nitride $Fe_4N(\gamma')$ directly precipitates from austenite.

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Scope of Research in Micro-Metallurgy at the National Metallurgical Laboratory

B. R. Nijhawan

AMONGST some of the diverse facets of fundamental researches and equally dispersed themes of applied research in metallurgical fields, the subject of "micro-metallurgy" perhaps provides the "missing link"—missing in the sense that it has relatively escaped the metallurgical limelight, even though unobtrusively providing the "link" between theory and practice in the growth of vast array of specialized ferrous and non-ferrous alloys in current usage. The major effects upon metals and their alloys of minute changes in their composition both additive and the reverse in terms of serious damage or of equal metallurgical benefit, have provided the base for some major fundamental research studies besides providing the pattern for the "applied" development of multitude alloys of inestimable value to the growth of modern engineering industries in this jet and space age. The mechanism of how so much is conferred by the so minute and the recurring explanations, theories and hypotheses, present to the theoretical scientist and practical metallurgist a fascinating metallurgical spectrum of endless research activity and applied development work. The National Metallurgical Laboratory during a decade of its activity, has ventured into fields unknown and sought to further explore those well-known.

In embarking upon any major research programme, the available technical literature invariably presents an array of loosely dispersed and scattered references on the subject; in the process of cataloguing the technical and research data available on the subject, one comes across fields offering potential scope for original research studies as also others for studying known hypotheses on the subject with a view to their application ultimately for the development of a new family of alloys. The work at the National Metallurgical Laboratory has been no exception to this general rule. Even though attention was drawn to the subject a decade back at one of the NML Symposia, and work pursued since, much more distinctly remains to be done in specialized fields of micro-metallurgy. Research and development work at the National Metallurgical Laboratory have so far covered the following scope, empirical perhaps in its application but scientifically sustaining none-the-less :

a. Effects of micro-additions on grain-size control of steel.
b. Abnormality in steel in relation to micro-metallurgy.
c. Strain-ageing of steel and effects of boron and nitrogen thereon.
d. Micro-additions of rare earths to stainless steels.
e. Rare earths and their micro-additions to Al-Mg alloys.
f. Micro-metallurgy of Al-Si alloys.
g. Carbides and nitrides in low alloy steels.
h. Effects of trace elements on the ageing of aluminium-copper alloys.
i. Micro-metallurgy of liquid metals.
j. Micro-additions to heat resistant alloys.
k. Analytical techniques for the determination of micro-additions.

The planning of research studies in the above fields calls for an analytical approach in assigning priorities even though some of the themes are self-sustaining once in their tracks provided relevant specialized research equipment, accessories and facilities maintain an unhindered flow. Researches in these fields of theory and practice can practically be endless and the last word can hardly be claimed on the subject and yet the results obtained have been well rewarding in applying the research techniques analytically with well defined objectives. Work in these directions will indeed be unending, unfolding the effects of micro-additions on metallic alloys, their causes and effects. A general outline of the work at the National Metallurgical Laboratory will now be given along with current thinking on the subject in each case.

a. Effects of micro-additions on grain-size control of steel

Initial work on the subject formed the subject of the first Monograph of the National Metallurgical Laboratory entitled 'Austenitic grain-size control of steel'[1] outlining the effects of micro-contents of aluminium to grain growth inhibition and their effects on the physical properties of plain carbon steels; identical work was thereafter carried on nickel-chrome steels.[2] It has been found that micro-content of aluminium is the one single most important factor in imparting requisite grain growth characteristics to steels. Chatterjea and Nijhawan[3] studied the physical properties and grain growth characteristics of a large variety of steels made under identical conditions. Despite the voluminous data on the subject, the exact mechanism of the phenomenon of grain growth

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Dr B. R. Nijhawan, Director, National Metallurgical Laboratory.

inhibition in steels has not been fully elucidated. The hypothesis based on submicroscopic Al_2O_3 particles, residual aluminium contents, surface absorption, the roles of aluminium sulphide and aluminium nitride as inhibitors to austenitic grain growth were critically examined. It was found that hypothesis based on the presence of submicroscopic Al_2O_3 particles or intergranular sulphide inclusions could not explain the observed grain growth characteristics of grain refined steels. It was observed that on soaking in nitrogen atmosphere, intergranular precipitation of aluminium nitride occurred in steels containing residual micro- and macro-aluminium contents. In nitrogen soaked specimens, the size and distribution of precipitated aluminium content, and the precipitated phase tended to agglomerate at higher heat-treating temperatures. The grain coarsening temperature agreed fairly well with the solution temperature of AlN. It was observed that the precipitation and resolution of submicroscopic aluminium nitride in steels with optimum residual aluminium content and the agglomeration of the aluminium nitride in high aluminium steels could account for the observed grain-coarsening characteristics of aluminium killed steels.[4]

Micro-additions of aluminium and nitrogen to steels exercise significant effects on their austenitic grain growth characteristics and physical properties. Effects of such micro-additions judiciously made, in relation to the properties, isothermal transformation characteristics, MS points and grain-growth characteristics of steels were studied. Grain refinement enhanced the impact toughness without affecting the tensile strength of some plain carbon steels. In nickel-chrome steels, grain refinement lowered the suscepitibility to temper-brittleness. The phenomenon of abnormal grain growth was comprehensively investigated and earlier hypotheses based on the role therein of submicroscopic Al_2O_3 particles, residual aluminium and aluminium sulphide were found untenable. Intergranular precipitation was observed on soaking the steels in nitrogen and the precipitated phase was identified to be aluminium nitride. The aluminium nitride contents of the steels decreased with the rise in temperature. The solution temperature of aluminium nitride in the austenite fairly agreed with the grain-coarsening temperature of the steels. In steels containing optimum micro-addition of aluminium, isothermal grain growth below the grain coarsening temperature was not conspicuous. The size, distribution and agglomeration of AlN at higher temperatures were significantly affected by the residual aluminium contents of the steel. It was established that in steels containing optimum aluminium content, the precipitation of AlN provided the requisite grain growth inhibition whilst its solution led to abnormal grain coarsening. The agglomeration of AlN in high aluminium bearing steels caused the reversion to normal grain growth behaviour. Some results of electron-diffraction studies of steels containing micro-contents of aluminium following nitrogen treatment, established the sub-microscopic precipitated phase to be AlN—an observation which finds very scanty reference in the technical literature on the subject.

X-Ray diffraction data of the extracted AlN from 1·5% Al steel, along with a diffractograph of the extracted residues taken in CuKα radiations are given in Tables I, II and III, and in Figure 1.

Some electron microphotographs of the Al-killed steel samples showing AlN particles at the grain boundaries are given in Figures. 2,3,4.5, and 6. The steel samples contained 0·04% and 0·06% aluminium. These were decarburized, nitrided in nitrogen for 4-5 hours and then homogenized at 650°C in vacuum for 10 hours followed by quenching in iced brine. The samples were polished mechanically and nital etched. Immediately after etching the fresh samples, 'Formover' replicas were dry stripped, which were examined in the electron microscope. Figure 2 shows an electron micrograph of a ·06% Al steel showing aluminium nitride particles (black) and the sites of the particles (white) on a 'Formover' replica, dry stripped from an etched steel surface. Figures 3,4,5 and 6 also show the dispersion of aluminium nitride particles in different samples (same heat treatment) with greater magnifications. For the preparation of the Al-killed steel samples, the procedure given by C. C. Hsiao[5] was followed. However,

TABLE I AlN (3-1144)

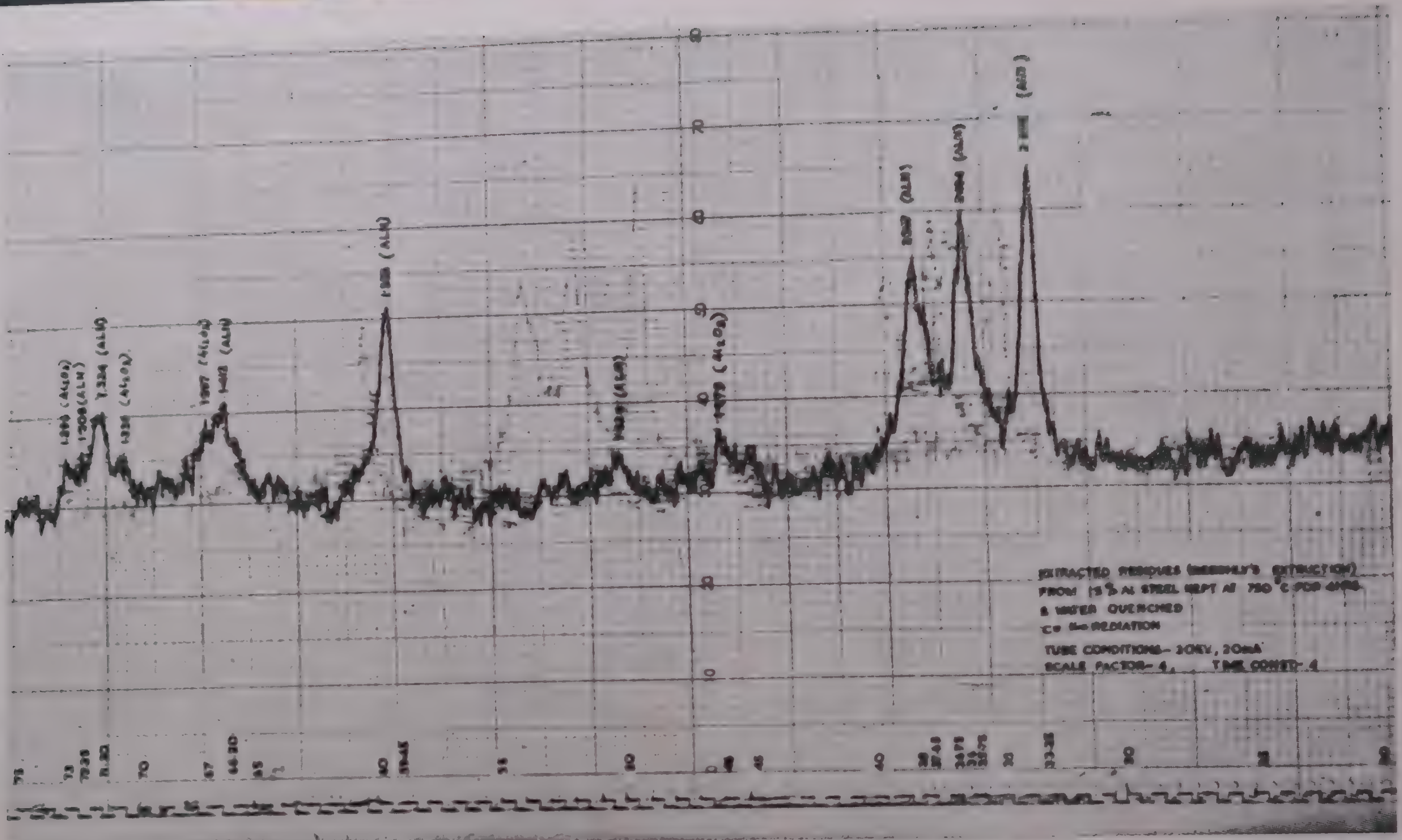
A.S.T.M. Data		X-ray diffraction data of the extracted residues from 1·5% Al steel nitrided at 1050 C and water quenched (diffractrometric study) CuKα	
d — Å	I/I$_1$	d — Å	I/I$_1$
2·70	90	2·690	91·6
2·49	80	2·488	50·0
2·36	90	2·367	58·3
1·83	50	1·985	59·0
1·56	100	1·832	5
1·42	100	1·817	2·5
1·35	40	1·554	42
1·33	100	1·500	2·5
1·31	70	1·401	100
1·19	50	1·380	20
1·13	20	1·318	10
1·05	80	1·301	6
1·01	50	1·181	10
1·00	80	1·088	6
0·974	50	1·052	10
0·946	56		
0·938	80		
0·901	70		
0·871	100		
0·848	80		
0·803	90		

TABLE II AlN (3-1144)†

System, Hexagonal
$a_0 = 0·113$ — Å
$c_0 = 4·981$ — Å
Calculations for d-values and hkl (Based on the lattice parameters)

d — Å	I/I$_1$	(h, k, l)
2·6961	90	100
2·4926	80	002
2·3719	90	101
1·8294	50	102
1·5609		003
1·5575	100	110
1·4912		111
1·4142	100	103
1·3452	40	200
1·3200	100	112
1·3011	70	201
1·0452		203
1·0190	50	210
0·9982	80	211
0·9725	50	114
0·9434	50	212
0·9339	80	105
0 8988	70	300
0·8686	100	213
0·8392	80	115

† Jeffery & Parry, J. Chem. Phys, 23, 406, (1955)



1 *Diffractograph of the extracted residues taken in Cuk$_\alpha$ radiations.*

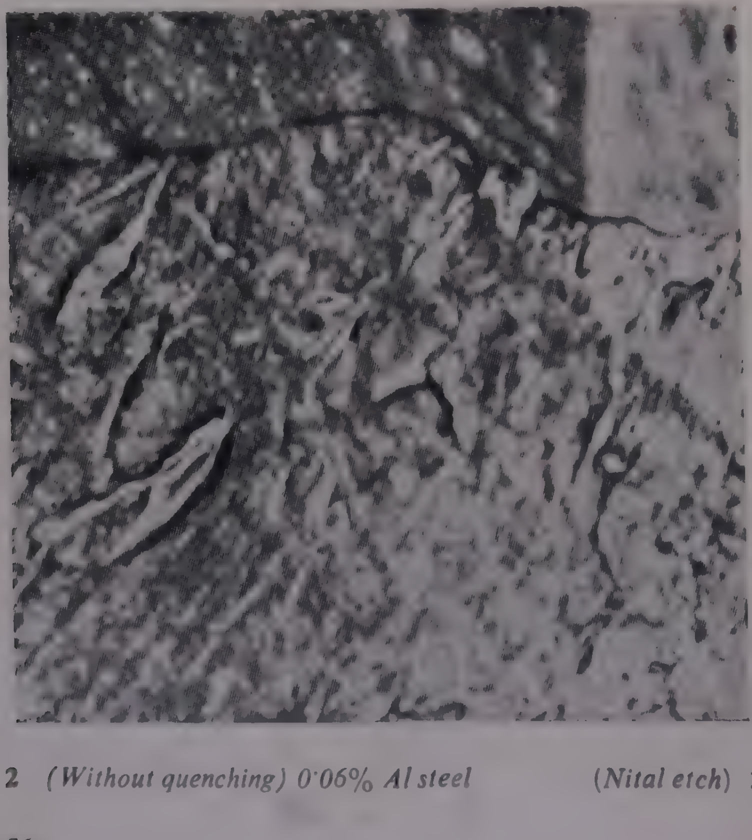
to examine the nature of the distribution of AlN particles at the grain bounderies at the austenitizing temperature, the samples were further soaked at 900°C and quenched in iced brine.

Electron-diffraction data of a steel containing 0·06% aluminium likewise treated as in the case of electron-micrographic studies, are given in Table IV, which shows that the specimen contained small amounts of AlN in the mild steel base. Figure 7 shows the electron-diffraction pattern from which the data were obtained.

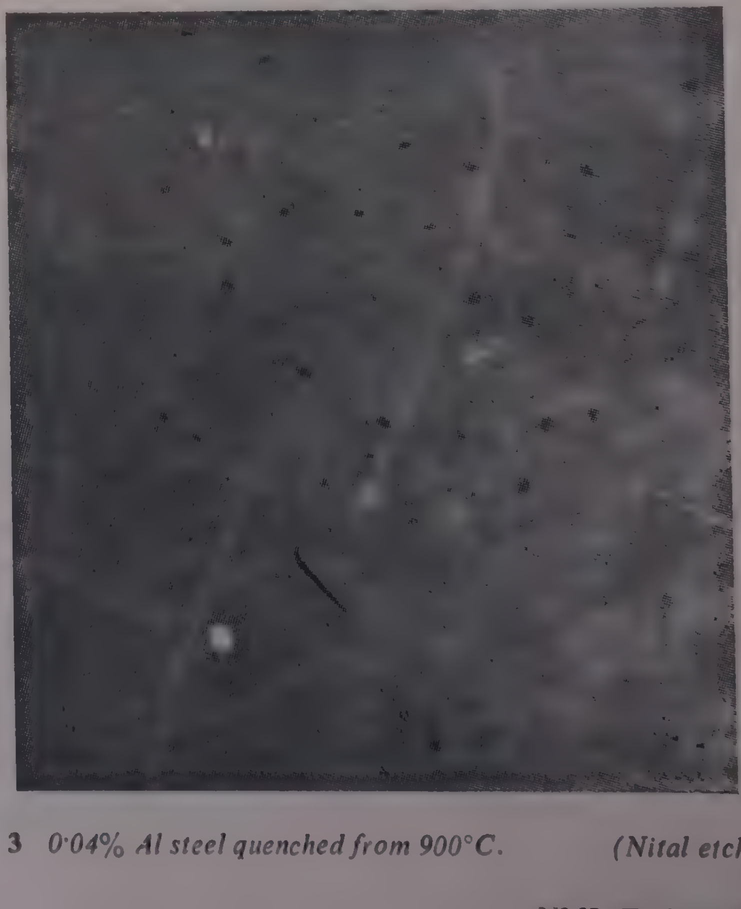
b. Abnormality in steel in relation to micro-metallurgy[6]

The subject of 'abnormality' in steels has of late, somewhat receded in the background, even though its

Electron Microphotographs of Al-killed steels (0·04 and 0·06% Al) 'AlN' particles at the Grain Boundaries (Quenched fram 909°C). Figs. 2 to 6



2 *(Without quenching) 0·06% Al steel* *(Nital etch) ×4 000*



3 *0·04% Al steel quenched from 900°C.* *(Nital etch) ×4 000*

TABLE III X-ray diffraction data of the extracted residues with standard values

d–A, for the extracted residues from			d–Å for the standard samples (A.S.T.M.)		
1·5% Al sreel nitrided at 1050°C. and quenched		0·4% Al steel nitrided and quenched from 1050°C			
Diffracto-metric study CuK$_\alpha$	11·46 Cm power camera CuK$_\alpha$	5·73 cm camera CuK$_\alpha$	AlN d–Å (I.I$_0$)	Fe$_3$N	Fe$_4$N
	2·845 (f)				
2·690 (91·6)	2·698 (vs)	2·711 (m)	2·70 (90)		3·79 (10)
2·488 (50·0)	2·492 (s)	2·478 (m)	2·49 (89)		2·684 (20)
2·367 (58·0)	2·378 (s)	2·367 (m)	2·36 (90)		
	2·285 (m)				
	2·158 (f)			2·19 (25)	2·091 (100)
	2·013 (f)				
1·985 (59·0)	1·995 (m)	1·987 (m)		2·09 (100)	
	1·9708 (f)				
					1·897
1·831 (5)	1·8355 (m)		1·83 (50)		
	1·6034 (vf)			1·61 (25)	1·697 (20)
1·554 (42)	1·554 (vs)	1·55 (m)	1·56 (100)		1·549 (20)
1·508 (2·5)					
1·497 (2·5)					
1·401 (100)	1·40 (vs)	1·40	1·42 (100)		
1·380 (20)	1·35 (m)		1·35 (40)	1·37 (25)	
1·318 (10)	1·32 (s)		1·33 (100)		1·342 (67)
1·301 (6)	1·3011 (m)		1·31 (70)		
				1·24 (25)	1·265 (20)
1·181 (10)			1·19 (50)		1·200 (10)
				1·16 (20)	
			1·13 (20)	1·14 (10)	1·144 (83)
1·088 (6)				1·10 (10)	1·095 (38)
1·052 (10)			1·05 (80)		1·053 (20)
	1·0394 (m)			1·04 (5)	
			1·01 (50)		1·014 (20)
	0·993 (m)		1·00 (80)		
	0·968 (m)		0·974 (50)		
			0·946 (50)		0·949 (44)
			0·938 (80)		
				0·92 (5)	
			0·001 (70)		
	0·8657 (s)		0·871 (100)	0·88 (8)	
	0·842 (s)		0·848 (80)	0.86 (8)	
			0·803 (90)	0·82 (3)	

practical importance has not diminished. Factors influencing abnormality are related to the micro-preseuc of aluminium, oxygen, nitrogen, etc. in hyper-eutectic zones of carburized steels; each of these factor has been well investigated. The degree of abnormality in different dapths of the case-carburized zone of the steel was observed to be affected by the supposed formation of Al_2O_3 as also possibly of AlN in the relevant zones. Carburization treatments with and without oxygen and nitrogen were carried out to substantiate some of the observations made. Steels containing micro-contents of aluminium optimum for austenitic grain-growth inhibition, were likewise investigated. The subject of 'abnormality' in steels which perhaps owed its origin to case-carburization treatments to promote high surface hardness and came to limelight following the presence of 'abnormal soft spots', is none-the-less important and interesting from both theoritical and practical standpoints, despite the development of alternative modes of surface-hardening other than case-carburization.

c. Strain-ageing af steel and effects of boron and nitrogen thereon

In commercial steels, nitrogen is important in promoting strain ageing. The precipitation of nitrogen by the addition of strong nitride forming elements such as, titanium or aluminium has been well established. Vanadium has also been found effective in eliminating strain ageing, but is an expensive addition. Morgan and Shyne[7] have demonstrated that boron can be effective in eliminating nitrogen strain ageing effects. In their study, effectiveness of boron in producing non-ageing rimming steel was achieved by closely controlling the excess oxygen content in the bath by the addition of aluminium. As aluminium itself being a strong nitride forming element, it was felt that the effect of boron in promoting non-ageing effects could be confined, if identical effect was noted when the steel of the same composition, was treated with ferro-silicon to control the excess of oxygen instead of with aluminium.

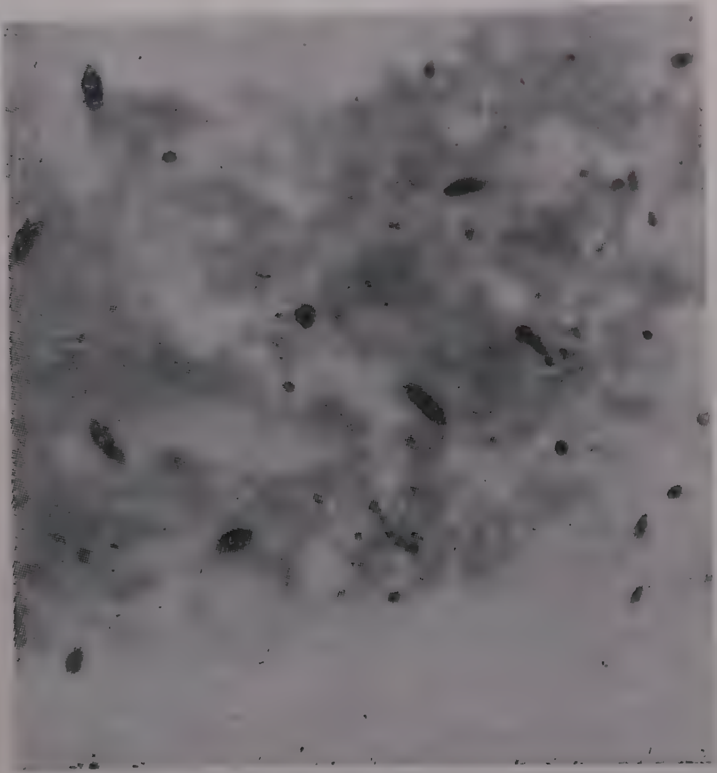
In the work done, steels of the following composition were studied with the addition of 0·004% to 0·009% boron. Silicon contents of steel were also changed from 0·023% to 0·1%.

Chemical Composition

C	—	0.04%
N	—	0.009 — 0.01%
Mn	—	0.022 — 0.024%
Al	—	Trace

All the heats were melted in the high frequency furnace. Carbon content of the metal was adjusted by the additions of graphite to the low carbon steel in the melt while ferro-silicon and ferro-boron were added to the

4 *0·06% Al steel quenched from 900°C.* *(Nital etch)×8 000*



5 *0·04% Al steel quenched from 900°C.* *(Nital etch)×16 000*

ladle and stirred well. The metal ingot was reduced to 1/8″ thick plates by hot forging and rolling. Specimens of 1/2″ sq. were used from the plate for quench ageing experiments and standard tensile specimens of 2″ gauge length were cut from the plate strain ageing experiments. After normalizing the specimens were quenched from 900°C and kept for different periods varying from 1 hour to 6 months. For studying strain ageing effects, normalised specimens were strained to 5% elongation and were aged for the same periods.

It was observed that the maximum non-ageing effect in the boron treated steel samples was observed with approximately 0·006% boron when the silicon content was about 0·08% in the case of both strain ageing and quench ageing. With the same percentage of silicon, the rimming behaviour of the steel was observed to be quite satisfactory. With higher additions of boron to about 0·008 and 0·01%, the rimming response of the steel was reduced. On the other hand, the lowering of silicon to 0·04% or 0·06% failed to impart the non-ageing characteristics in the steel samples even when the boron content was raised upto about 0·008%. In steel samples containing boron content of about 0·01%, difficulty was experienced in forging and rolling as those samples were prone to hot-cracking.

TABLE IV
0·06% aluminium.

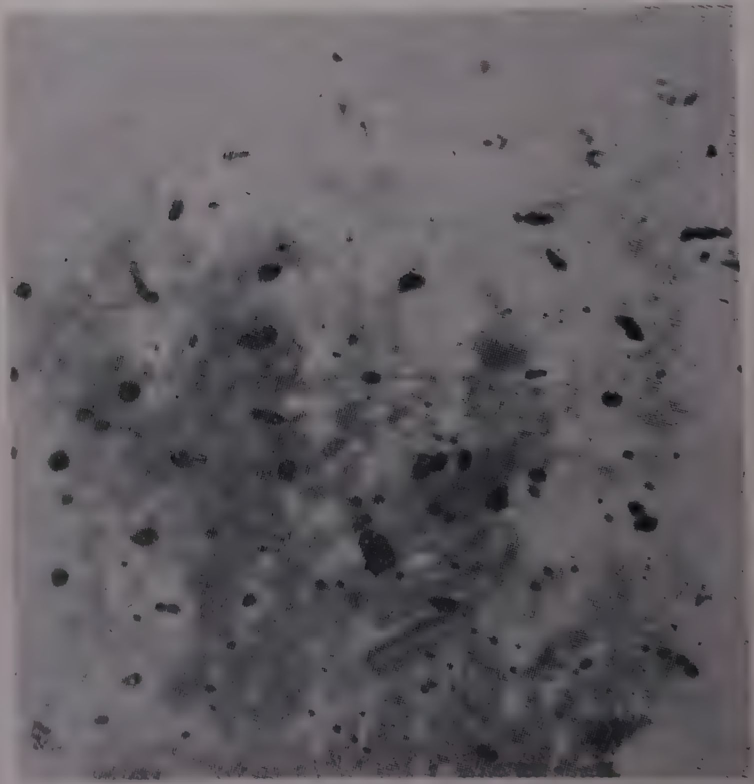
Intensity visual	ring radium (r) cm	$d=\frac{\lambda l}{r}$ A	X-ray data Fe A	AlN* A	hkil
ms	0·755	1·987	2·02	1·98	
s	0·980	1·530	(1·43)	1·55	1120
m	1·256	1·194	1·17		
f	1·425	1·05	— (1·01)	1·05	2023
s	1·590	0·943	—	0·9134	2132
vf	1·685	0·890	0·91	0·8988	3030
mf	1·790	0·838	0·827	0·839	1125
f	2·037	0·736			
vvf	2·290	0·656			
vvf	2·590	0·577			

* ASTM X-ray data card No. 3-1144.
s—strong, m—medium, f—faint, vf—very faint,
mf—medium faint, vvf—very very faint, ms—medium strong
l=1·50 Acm obtained from a graphite pattern.

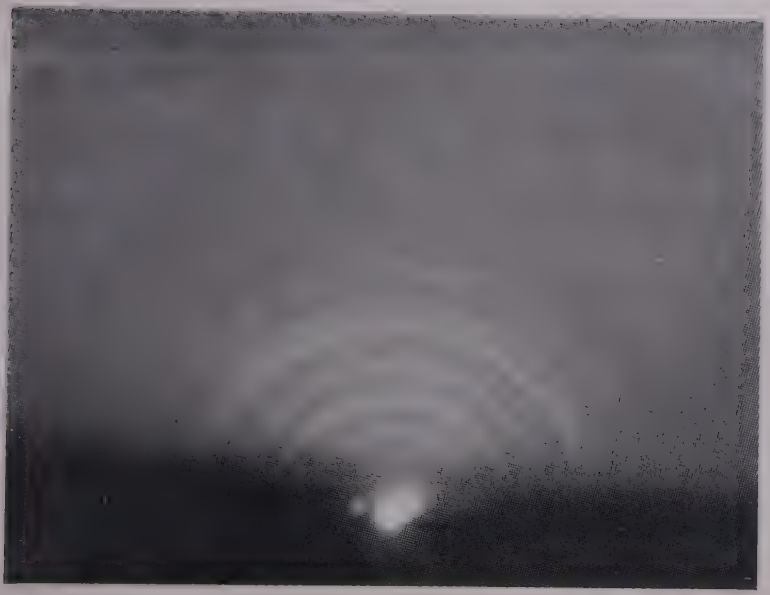
d. Micro-additions of rare earths to stainless steels

Highly alloyed austenitic snainless steels possess poor hot workability. The deficiency is aggravated with the increasing ingot size. Although some improvements have been obtained by the addition of deoxidizing ferro-alloys containing aluminium and titanium to the steels, micro-additions of rare earth metals and their oxides showed the most remarkable effect in this direction.

Hanke and Lula[8] showed that best results could be obtained by the addition of 4–5 lb of metallic rare earths



6 *0·06 Al steel quenched from 900°C.* *(Nital etch)×1 6000*



7 *Electron-diffraction pattern from a steel sample containing 0·06% aluminium.*

per ton of steel. Such treatment, however, resulted in the formation of certain type of inclusions and surface cracks. Successful results were obtained by addition of 3 lb of rare earth metal oxides per ton of steel following deoxidation of the steel with ferro-alloys containing aluminium and titanium.

Addition of misch metal to austenitic stainless steels which are not particularly difficult to hot work, increases the ingot to slab yield by 6 to 12%. A residual rare earth metal content of only 0·02 to 0·05% in the steel is required to bring about the improvement. The beneficial effect of rare earth metal addition, however, is most evident in the highly alloyed steels that are exceptionally difficult to hot work such as 20% Cr, 26% Ni, 3% Mo, 3% Cu steel; a higher residual rare earth content of 0·2% is required in such cases.[9]

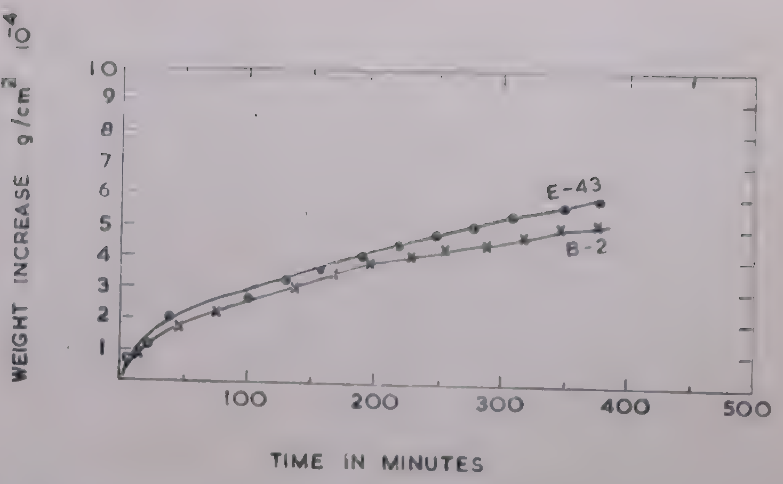
The mechanism of improvement in the hot working property of the austenitic stainless steels by the addition of rare earth metals and oxides has been related to various factors such as (1) effective deoxidation of the melt, (2) prevention of hot shortness caused by sulphur and (3) counteraction of the harmful effects of the residual elements such as lead, tin and silver which impair the hot working property of the steels.[9]

Effects of rare earth additions on hot working characteristics and oxidation resistance of nickel free austenitic chromium-manganese-nitrogen stainless steel were investigated at length. Cerium misch metal was added to the stainless steel with the composition of chromium 21%, manganese 14% and nitrogen 0·70%, obtaining a cerium content of 0·02 to 0·04%. Misch metal addition, however, did not result in any appreciable improvement of hot working property in the case of nickel-free austenitic stainless steels studied.

Oxidation resistance tests at 900°C were conducted in an atmosphere of dry oxygen on samples of heat No. E-43 containing 0·04% cerium. For comparison, tests were also performed on samples of heat No. B-2 which had a similar composition as E-43 but contained no cerium. Compositions of the heats are given below :

Heat No.	Cr%	Mn%	N%	C%	Ce%
E-43	20·33	14·36	0·56	0·04	0·04
B-2	20·9	13 8	0·68	0·12	nil

Results of the tests, shown in Figure 8, indicated the same order of oxidation rate at 900°C of the cerium treated and the untreated nickel-free austenitic stainless steels.



8 *Graphic results of oxidation resistance tests at 900°C of cerium treated and untreated steels.*

e. Rare earths and their micro-additions to Al-Mg alloys

Light alloys of aluminium containing magnesium, which are characterised by their high resistance to corrosion in certain media, high tensile strength values at room and elevated temperatures and good machinability are not normally hot-workable when their magnesium content rises above 6%. Our earlier work[10] showed that aluminium-magnesium alloys with magnesium ranging from 7-10%, could be made hot workable by the additions of 2-3% of misch-metal. Addition of misch-metal was found to change the as-cast mircrostructure, inasmuch as the β Al-Mg phase was progressively eliminated and new phases essentially containing cerium were precipitated. The tensile strength of the as cast Al-(7–10%) Mg alloys was found to dercrease by the addition of 2–3% misch-metal above which it again showed a rise. The tensile strength of the wrought specimens continued to rise with increase in the amount of misch-metal added.

It is known that, even though the solubility of magnesium in aluminium falls steeply from 15·53% at 450°C to about 1% at room temperature, alloys with magnesium content as high as 10% show an abnormally small response to age hardening. Work was undertaken at the National Metallurgical Laboratory to study the effects of small additions of misch-metal, silver and copper on the age-hardening characteristics of Al-(7-10%) Mg alloys. It was observed that the addition of misch-metal upto 3% did not have any significant effect on the elevated temperature age-hardening characteristics of these alloys. Room temperature ageing determined on the basis of tensile-strength and 0·1% proof stress, showed that both these values were improved over a period of about two years. Silver and copper did not appear to improve the hardness of these alloys when aged at 250°C for as long as 1000 hours. However, the tensile strength was either not affected or was raised with the micro-additions of silver, but was lowered when small additions of copper were made to the alloys.

f. Micro-metallurgy of Al-Si alloys[11]

Hypo-and hyper-eutectic aluminium-silicon alloys find almost universal applications to-day in almost every branch of engineering industry. Excellent casting characteristics, corrosion resistance and ductility of the hypo-eutectic alloys, good anti-friction properties, high thermal conductivity and good wear resistance of the hyper-eutectic alloys render them highly suited in the automobile industry for the manufacture of pistons, brakedrums, cylinder heads and cylinder blocks etc. However, the coarse needlelike flakes of silicon in hypo-eutectic alloys, and segregated coarse primary silicon particles in hyper-eutectic alloys restrict their industrial utility owing to the effects of the coarse structure on machinability, surface finish tool life, etc. Hypo-eutectic aluminium-silicon alloys are modified by sodium and hyper-eutectic alloys by phosphorus; whereby considerable improvement in the microstructure and mechanical properties are effected. However, these two modifying agents have their limitations. Sodium modifies the eutectic in hypo-eutectic alloys but fails to modify the eutectic in hyper-eutectic alloys. Similarly, phosphorus in hyper-eutectic alloys only refines the primary silicon particles leaving the eutectic unaffected. No single modifying agent has hitherto been found which simultaneously modifies and refines both the primary silicon and the eutectic. This aspect was investigated at length in the National Metallurgical Laboratory. It was observed that sulphur when present to the extent of 0·01% in the aluminium-silicon alloys modified the alloys both in the hypo-and hyper-eutectic ranges. It was also observed that the effect of sulphur was enhanced if phosphorus was also present in the hyper-eutectic alloys. Aluminium-silicon alloys modified by sulphur exhibited spectacular improvement in the fluidity, machinability and surface finish in addition to significant improvements in the micro-structure.

Table V gives the mechanical properties and fluidity of an aluminium–9% silicon alloy and aluminium–23% silicon alloys, after treatment with various modifying agents developed at the National Metallurgical Laboratory.

The micro-photographs of the aluminium-silicon alloys in the unmodified and modified conditions are given herewith along with those of fluidity pattern castings (Figs. 9–17).

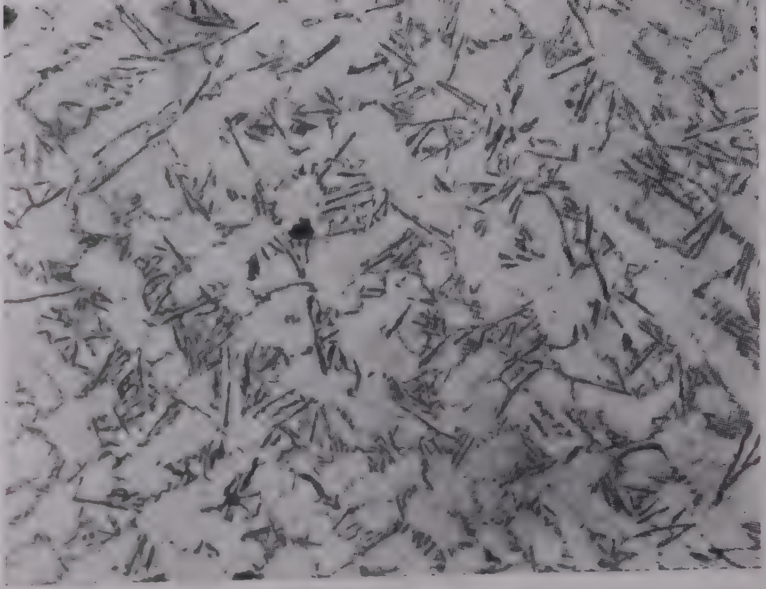
TABLE V

Mechanical properties and fluidity of an aluminium—9% silicon alloy, and aluminium—23% silicon alloy, after treatment with various modifying agents.

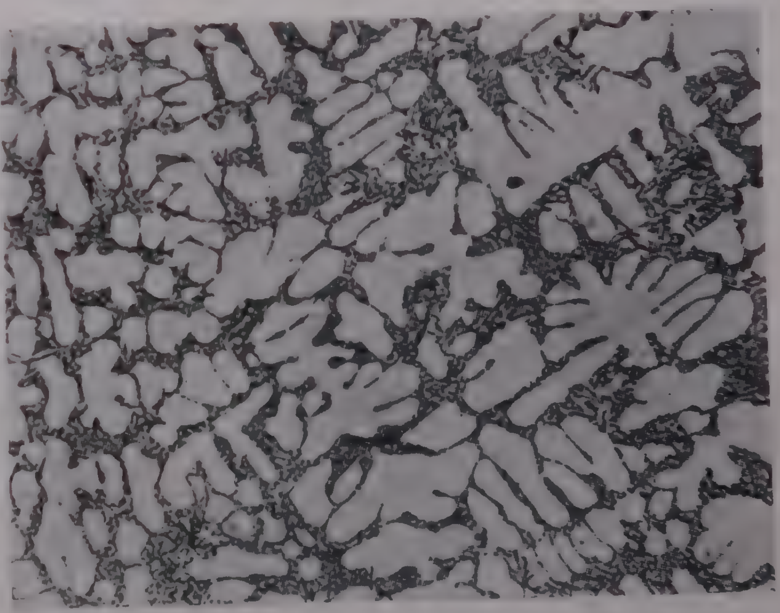
Composition	Condition	Mechanical properties			Fluidity
		Tensil Strength Tons/sq. in (Kg/sq.mm)	B.H.N.	%Elongation 2″ G.L. (50.8 mm)	Casting Inches (mm)
9·15% Si 0·70% Fe	Unmodified	7·4 (11.7)	50	3	23 (584)
9·15% Si 0·70% Fe 0·012% S	Modified by sulphur	7·8 (12·3)	58	6	35 (889)
23·55% Si 0·68% Fe	Unmodified	6·0 (9·5)	115	Nil	29 (736)
23·50% Si 0·70% Fe 0·01% P	Modified by Phosphorus	7·2 (11·3)	100	Nil	38 (965)
23·47% Si 0·65% Fe 0·011% S	Modified by sulphur	8·7 (13·7	110	Nil	62 (full) (1575)
23·50% Si 0·70% Fe 0·011% P 0·009% S	Modified by phosphorus and sulphur	8·5 (13.4)	120	Nil	62 (full) (1575)

g. Carbides and nitrides in low alloy steels.

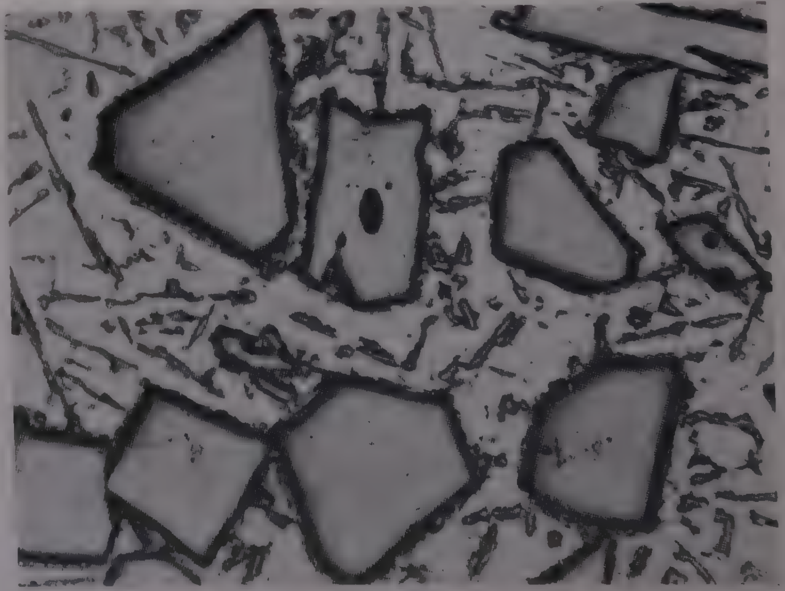
This nature and structure of the precipitated phases in chromium-maganese-nitrogen steels containing 18-22% chromium, 12-14% manganese, 0.4-0.8% nitrogen and



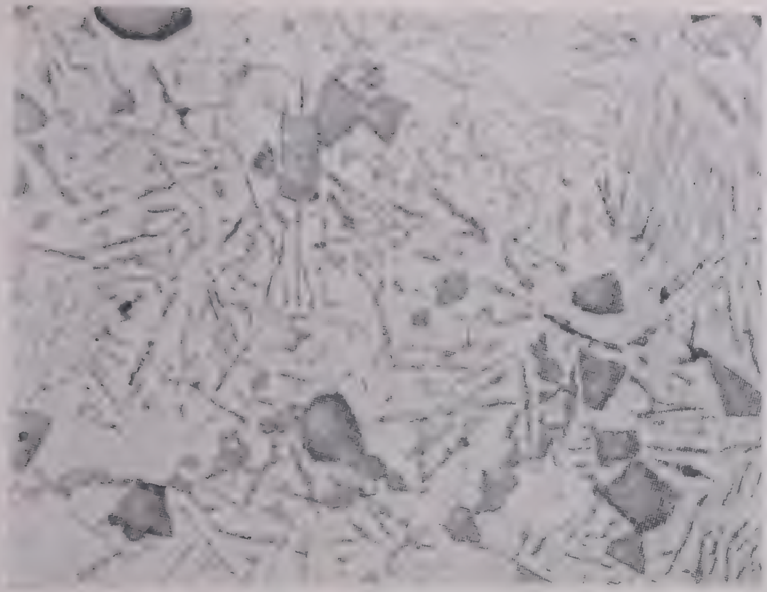
9 *Photomicrograph of aluminium—9% silicon alloy, unmodified* ×*150*



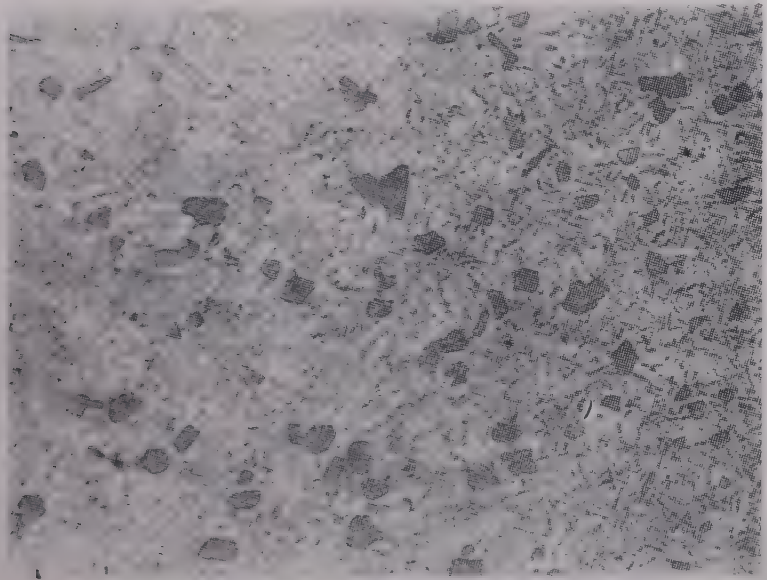
10 *Photomicrograph of aluminium—9% silicon alloy, modified by sulphur.* ×*500*



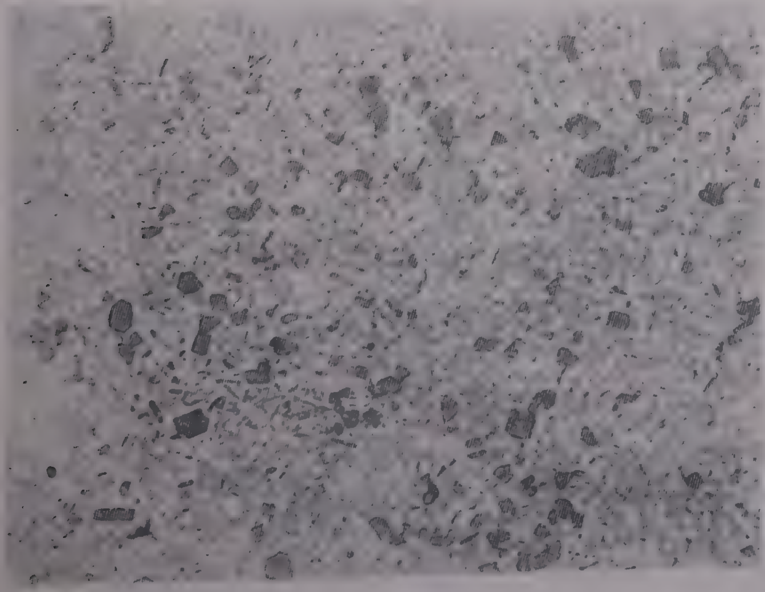
11 *Photomicrograph of aluminium—23% silicon alloy, unmodified.* ×*150*



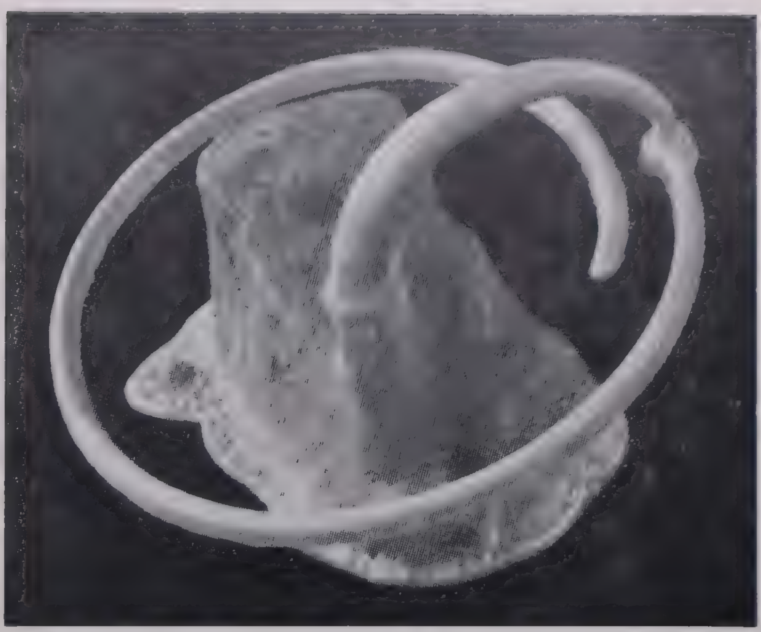
12 *Photomicrograph of aluminium—23% silicon alloy, modified by phosphorus.* X150



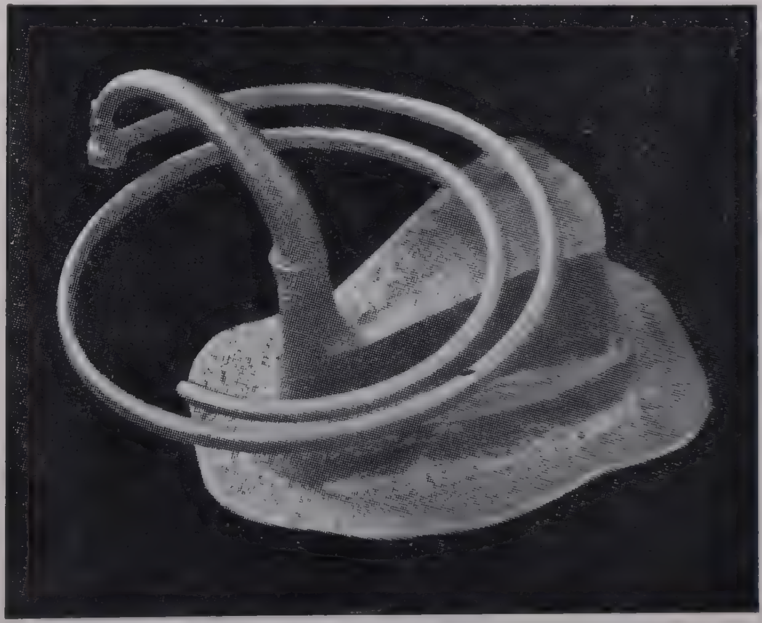
13 *Photomicrograph of aluminium—23% silicon alloy, modified by sulphur.* X150



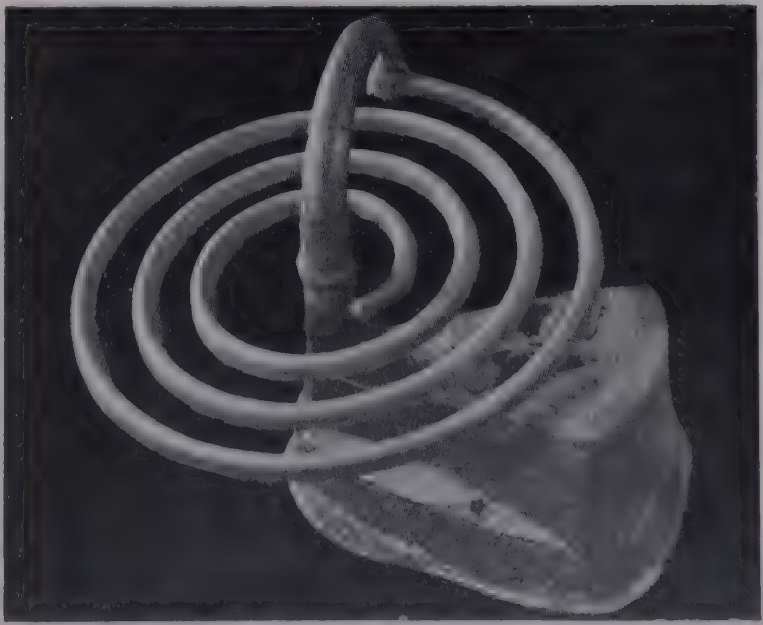
14 *Photomicrograph of aluminium—23% silicon alloy, modified by both phosphorus and sulphur.* X150



15 *Fluidity pattern casting of aluminium—23% silicon alloy, unmodified.*



16 *Fluidity pattern casting of aluminium—23% silicon alloy, modified by phosphorus.*



17 *Fluidity pattern casting of aluminium—23% silicon alloy, modified by sulphur.*

0.05-0.3% carbon, during sub-critical ageing and cold working have been studied using mainly X-ray diffraction and spectroscopic analyses.

The stability of the austenite phase after solution treatment at 1050°C and sub-critical ageing at temperature between 500°C-800°C and also after cold working was studied by in situ X-ray diffraction examination of the treated samples. The precipitated phases formed during ageing at the stated temperatures, were also studied after isolating them by electrolytic and/or chemical methods.

The austenitic phase in chromium-manganese-nitrogen steels studied remained stable upto 30-40% of cold reduction. With further cold working a. b. c. c. phase, having a lattice parameter of 2.868 Å was observed ; this phase change was similar to the transformation taking place in 18% chromium, 8% nickel austenitic stainless steels on cold-working but unlike Hadfield austenitic manganese steels.

The continuous decrease in the lattice parameter of austenite observed during sub-critical ageing indicated the decrease in the solute atom concentration of the matrix during ageing. Cr_2N and $Cr_{23}C_6$ types of precipitates were observed during ageing treatment on the carbon or nitrogen content of the steel. With carbon/nitrogen ratio in steels below 0.01, only Cr_2N was identified for sub-critical temperature ; whilst with a ratio above 0.3 carbon/nitrogen, Cr_2N and $Cr_{23}C_6$ were observed above 500°C and only $Cr_{23}C_6$ was noted at temperatur lower than 500°C. For ratio of 0.1 to 0.3 of carbon/nitrogen, the precipitated products showed only Cr_2N at temperature above 500°C while Cr_2N and $Cr_{23}C_6$ were observed below 500°C.

The activation energy of the formation of Cr_2N type of precipitate during ageing was determined, which showed slight increase in the value with the progress of the reaction i.e. decrease in the solute atom concentration. The value was found to vary between 33.85 to 38.71 kCal gm.mol.

The matrix remained austenitic after prolonged sub-critical ageing and no ferrite was detected, probably due to the fact that nitrogen retained in solid solution even after such ageing treatments, was sufficient to stabilize the austenite phase.

h. Effects of trace elements on the ageing of aluminium—copper alloys.

Work on some aspects of age-hardening was taken up with a view to ascertain the effect of specimen size, quenching medium, interrupted quench, reversion treatment and plastic deformation on natural and artificial ageing of aluminium-copper alloys. Effects of these variables were explained and rationalized on the basis that concentration of quenched-in vacancies played dominant role in age hardening of an alloy. It was shown that any process which increased the concentration of vacancies also accelerated the ageing and vice versa. The quenched-in vacancy hypothesis was applied to explain the effect of small amounts of impurities (∼0.1%) like tin, indium, cadmium, etc. on natural and induced ageing.[12] These impurities slowed down natural ageing and accelerated the ageing at high temperatures.[13] It was proposed that the impurity atoms associated themselves with thermally generated vacancies and the vacancy-impurity complex was stable at room temperature because impurities (In, Sn, Cd) with larger atomic diameter than aluminium would find themselves, in a position of minimum when associated with a vacancy. Thus, some vacancies became inoperative and were not able to activate diffusion of copper atoms.

Indirect support for these views was provided by the close similarity of the effects of impurities and reversion treatment on the subsequent age hardening of aluminium-copper alloys at room and elevated temperatures.

i. Micro-metallurgy of liquid metals[14]

Significent strides made in the limits of resolution in electron microscopy, and new experimental techniques developed reveal that important changes in the properties are brought about by clustering of solute and solvent atoms on the parent lattices, without the appearance of a separate phases. Clustering is a departure from at-random distribucion and frequently occurs prior to precipitation of microscopically resolved phases. Although experimental evidence is as yet not fully available, clusters are also believed to exist in the liquid state and are known as cybotactic, quasi-crystalline or quasi-molecular groups or kindered nuclei. Although liquid state of metals is the starting point of most metallurgical alloys, it has not received adequate attention commensurate with its importance. Our knowledge about the structure of melts is not specific corresponding to that for crystalline solid metallic state. A melt may be regarded as consisting of the following :

(1) Solid-like domains or clusters of short range order in oscillartory motion around an equilibrium position.

(2) Domains having random location without any equilibrium position and having gas like degrees of freedom.

(3) Fluidised vacancies or holes which dart around, rotate, colloid and interact much the same way as do the real molecules of a gas.

Thermo-dynamic equilibrium exists between (1), (2) and (3) at any instant. If a liquid metal is rapidly cooled, the vacancies may be retained in the form of dislocation loops and sub-electron-microscopic cavities and may be in excess of their equilibrium distribution in the solid state. The structure of liquid alloys may be regarded on a similar basis with the difference that the clusters may be of like atoms or of unlike atoms. Considering the clusters or the solid like domains as colloidal spherical particles, a liquid metal centrifuge was designed at the National Metallurgical Laboratory to detremine their size. Their size in Pb-Sn melts was found to vary between 25-55 Å when the temperature was raised to 700°C. The increase in the size of the clusters is not easy to explain at least in terms of fundamental thermodynamics but may be the first step towards liquid immiscibility observed in certain systems at elevated temperatures. During solidification, the clusters act as a forerunner of the nuclei of the solid phase. When the cluster size at temperature is such that it exceeds the size of the critical nuclei near the freezing temperature, no super-cooling of the melt may be observed ; this conclusion was confirmed in the N.M.L. studies on the Pb-Sn system.

j. Micro-additions to heat-resistant alloys[15]

In the course of comprehensive studies on the development of suitable alloys for electrical heating elements free of nickel and cobalt and wholly based on indigenous raw materials, extensive work was carried out on Fe-Cr-Al system of alloys covering the range 10-25%

Cr and 3–8% Al to which minor additions of Zr, Ti and misch-metal were made. It was confirmed that these minute additions played an highly important role in improving the metallurgical properties of the alloy. The hot working and cold workability or the alloys konwn to be difficult, were consideraly improved and the alloys were fully amenable to working with moderate ease by the small additions Zr, Ti and misch-metal. The scaling resistance of these alloys determined by the accelerated life test by electrically heating under 2 min. on-off condition was found to be superior in relation to alloys without the minute rare earth addition. The increase in weight method of assessing scaling resistance showed that the alloys containing micro-additions of rare earths got initially somewhat more oxidized but finally the oxidation rate slowed down perceptibly in comparison with corresponding alloys containing no rare earth additons. The rate of grain growth was found to be consipicuously inhibited by the additions of Ti, Zr and the rare earth addition which resulted in significantly improved high temperature properties. Basing on these investigations at the N.M.L., optimum alloy compositions with the above stated minute additions have been developed at the National Metallurgical Laboratory for high temperature electrical heating elements which will go into industrial scale production in the country based on the NML licensed processeses and production techniques.

k. Analytical techniques for the determination of micro-additions.

(*a*) *Spectrographic determination of boron in steel by rotating electrode method*:[16]

Boron is added to steel in minute amounts to improve its hardenability. In view of the low concentration of boron, accurate and rapid methods are required for its determination. A spectrographic method employing rotating electrode, high voltage intermittent A. C. arc and Hliger medium large quartz spectrograph for the determination of boron in steel has been developed at the N.M.L. Boron upto a lower limit of 0.001% was determined by this method by taking the steel samples into solution whilst synthetic standards having boron concentration ranging from 0.007 to 0.001% were used for preparing the working curve. Hilger large quartz spectrograph was used for recording the spectrum and Hilger non-recording microphotometer was used for measuremenr of the analytical line intensities. The accuracy of ± 5% of the amount present was obtained by this method.

(*b*) *Determination of smdll amounts of aluminium in steel* :[17]

Minute additions of aluminium made to the extent of 200 to 500 parts in a million to steels greatly improve some of their physical properties. A method has been developed at the N.M.L. for the determination of small amounts of dissolved aluminium (aluminium which can be dissolved in hydrochloric acid) in steel upto a lower limit of 0.005% by the spectrographic method.

Synthetic standards containing aluminium concentration ranging from 0.005 to 0.13% were used for preparing the working curve. Drillings of the test samples containing varying amounts of aluminium were taken into solution. Two drops of the solution were dried on the flat top of the graphite electrode and sparked by means of condensed spark of 8 KV. The spectra were recorded in Hilger medium quartz spectrograph and the intensities of the analytical lines were measured by Hilger non-recording microphotometer to prepare the working curve. The analysis lines Al 3082.16A and corresponding iron line Fe 3077.17A were used for the higher concentration of aluminium ; for lower concentration of aluminium (0.005 to 0.06%) aluminium line Al 3961.5A and corresponding iron line Fe 3969.109A were used. Results were obtained with standard deviation per cent varying from 10·2 to 4·0.

(*c*) *Simultaneous determination of copper and magnesium in zinc alloys for die casting* :[18]

Spectrographic determination of copper, alumtnium and magnesium was carried out by porous cup spark technique using synthetic standards and test samples in the form of solutions. Copper up to a lower limit of 0·008% and magnesium up to a lower limit of 0·005% were determined. The synthetic experimental standards contained copper 0·008 to 0·25% and magnesium 0·005 to 0·15%. Because of the difficulty in obtaining absolutely copper free zinc, determination of the residual copper in zinc used as matrix, was carried out first before the synthetic experimental standards were prepared. Exciation was done by high voltage condensed spark of 12 kV, added inductance 0·13 mH ; capacitance 0·005μF ; lower electrode was 6 mm dia carbon rod with 80° cone, whilst the upper electrode was a porous cup prepared by cutting a spec. pure graphite rod of 10 mm dia into 3·8 cm pieces and drilling a 3·4 mm hole in them along the axis from one end to within 1·25 mm of the other end. With pipette, 1 to 2 ml of the solution to be analysed were inserted into the cavity of this porous cup electrode and spark was run. During the sparking, the solution diffused through the porous electrode slowly by wick action constantly renewing the surface film of the solution. Hilger medium quartz spectrograph was used for recording the spectra and Hilger non-recording microphotometer was used for measuring the line intensities. An accuracy of percentage error varying from 0·5% to 7·5% of the amount present was obtained.

(*d*) *Determination of magnesium in nodular cast iron* ;[19]

Production of nodular cast iron requires a careful control of the percentage of the inoculant. For process control, the magnesium content in the melt should be estimated accurately and quickly. A small amount of magnesium up to a lower limit of 0·05% was determined by spectrochemical method employing standard metal electrodes. Upper electrode was a pure carbon rod of 6 mm dia tipped at 80° cone angle and the lower electrode was of the sample with a flat top. Excitation source was condensed spark of 12 kV. Hilger medium quartz spectrograph was used. Photometric measurement of the analytical line pairs of magnesium 2 802·7 and iron 2 783·69 A was made by Hilger non-recording microphotometer to prepare the working curve. Results of chemical and spectrographic analyses were also compared. Deviations from chemical method varying from 3–23% were obtained.

(*e*) *Determination of trace amount of antimony in lead-tin non-antimonial solder* :[20]

Estimation of antimony in solder by chemical method is cumbersome and often yields erratic results. A method was developed to estimate low amount of antimony up to 0·001 per cent in the lower side, in non-antimonial tin-lead solder by oxide arc technique. The technique provided for the determination of antimony from 0·001 to 0·1%. The dry oxide powder of the samples and standards synthetically prepared were mixed with pure graphite powder and put into the crater of graphite cup which served as the lower electrode and excited with direct current arc, the upper electrode being a carbon rod of 6 mm dia. with a flat top. The spectrum was recorded in the Hilger medium quartz spectrograph. Intensities of selected pairs of analytical lines of antimony 2 311-47A and lead 2 203·51A were measured photometrically to prepare the working curve. Analytical accuracy varied from 3–6% of the amount present.

(*f*) *Spectrographic estimation of impurities in pure tin*: Trace amount of impurities such as copper, lead, arsenic, antimony, zinc, silver, bismuth, cadmium up to a lower limit of 0 001% in pure tin samples were spectrographically determined using standard metal electrodes in a Hilger medium quartz spectrograph. Excitation of the spectra was obtained by spark discharge generated by simple condensed spark circuit. Upper electrode was spec. pure carbon rod of 6 mm dia. tipped at 80° cone; lower electrode was made up of the sample with flat top. Measurements of the analytical line densities of various impurities and the internal standard line of tin were carried out photometrically for preparing the working curve. The analytical lines for different elements present as impurities and the corresponding internal standard lines of tin were selected and the line densities were measured photometrically to prepare the working curves. The coefficient of variation of the results ranged from 2 to 10%.

The scope of research on "micro-metallurgy" is very vast indeed in its multitude implications and applications. The work so far carried out at the National Metallurgical Laboratory has given rewarding results whilst indicating useful fields for further research activity and programming in the context of available research facilities and equipment available for studying the mechanism, by which the so much is conferred by the so minute in terms of unanticipated benefits or hitherto unexplained damage to the resulstant metals and alloys. Research activity in such metallurgical spectra is almost unending and requires careful cataloguing of observed and less understood or inexplicable phenomena, and the formulation of useful family of special alloys in their wake and ultimate analyses, in the planning and execution of which, the National Metallurgical Laboratory is activeily engaged upon. Research and development work in these fields place high premium on scientific ingenuity and ability to observe, interpret and translate fundamental research results into applied themes of potential value; the luck also often befalls those most observant.

Acknowledgement

The author wishes to thank the research staff at the National Metallurgical Laboratory, references to whose scientific paper and reports have been made at the end of this paper and to Dr Y. N. Trehan and Dr J. K. Mukherjee for assistance in the electron and X-ray diffraction work.

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Naphtha Injection Trials at National Metallurgical Laboratory, Jamshedpur

THE National Metallurgical Laboratory has completed the installation of oil/light petroleum naphtha injection system for trials at the Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory.

Light petroleum naphtha is a by-product of Indian petroleum refining industry and is currently in surplus in India. Injection of light naphtha would be of considerable significance for iron smelting and it is with this objective, that trials on the injection of light petroleum naphtha have been initiated at the Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory.

Naphtha contains only 0.4%-0.5% sulphur compared to over 3.0% sulphur in furnace oil. The chemical characteristics of naphtha are given below :

TABLE I—Characteristics of naphtha

Density at 15°C g/ml	...
Sulphur wt. %	0.25 max.
Thermal value, Btu/lb (Gross)	20,200 min.
Cal/kg.	11,220 min.
Carbon/Hydrogen ratio	5–6

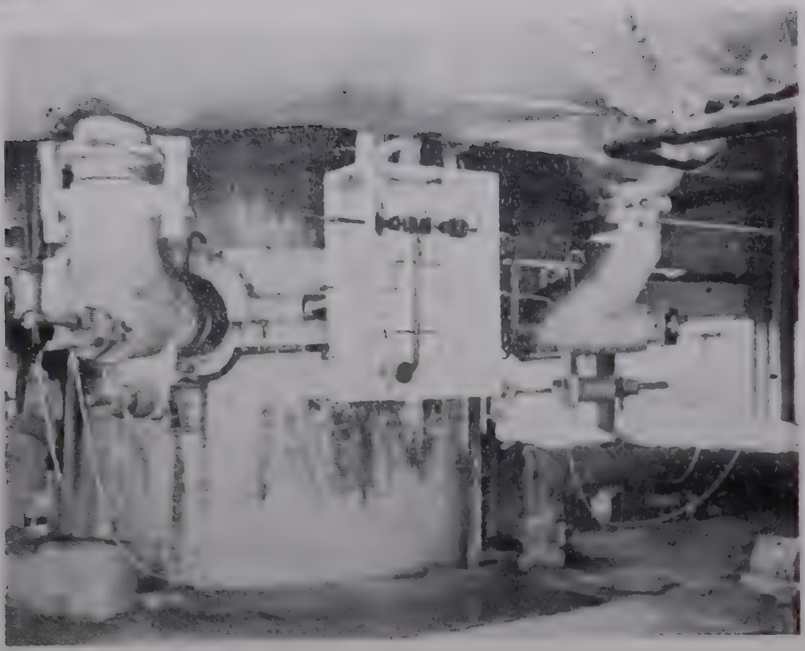
At the invitation of the Oil and Natural Gas Commission, the Institut Francais Du Petrole, Paris, made a survey planned for the development of petro-chemical industry in India in 1963. Their estimate of surplus naphtha available till 1971 classified annually is given in Table II.

TABLE II Estimated surplus naphtha available till 1971

Surplus naphtha after meeting motor gasoline demand in '000 tons	1966	1967	1968	1969	1970	1971
Digboi, Gauhati, Barauni	235	196	154	109	541	491
East India (Calcutta) Burmah Shell, Esso	657	637	617	594	570	860
Gujarat	258	249	258	550	540	529
Vizag	132	130	126	122	118	112
South India		131	424	424	408	392
Total	1106	1343	1575	1799	2177	2485

Light naphtha is stored in a 12 500 litres capacity underground storage tank provided with vent hole and an indicator for the quantity in the tank. Naphtha in the tank is subjected to a pressure of 1 kg/sq.cm. for its transfer from the underground storage tank to a 225 litres capacity service tank installed above the ground in the naphtha pump room. The naphtha injection lances are made out of two concentric stainless steel tubes, the inner tube carries naphtha at a pressure of 18 kg/cm sq. at the rate of 6–12 litres per hour. The space between the inner tube and outer tube is for passing compressed air at a pressure of 3 kg/cm sq, which besides cooling the naphtha lance, admits the requisite amount of air for the atomisation of naphtha through a suitably designed jet system. The naphtha is

1 *The 15 ton/day Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory.*



2 *Installation for light naphtha injection through the tuyeres of the Low Shaft Furnace Pilot Plant of the National Metallurgial Laboratory.*

kept at high pressure to prevent its vaporisation either in the lance or in the supply pipe line system.

The compressed air is supplied by a compressor operated with a 7·5 H.P. motor having a capacity of 20 cu ft/min at a pressure of 2 000 PSIG. It is provided with a 12 cu. ft. reservoir.

Oil pressure

Alarms, operated by pressure switches, indicate abnormal oil pressure at a lance if any, in the case of complete or partial blockage of oil passage in the lance or failure of the supply. Similar alarms indicate abnormal high/low air pressure at lances if any, in the case of failure of the air pressure regulator of compressors.

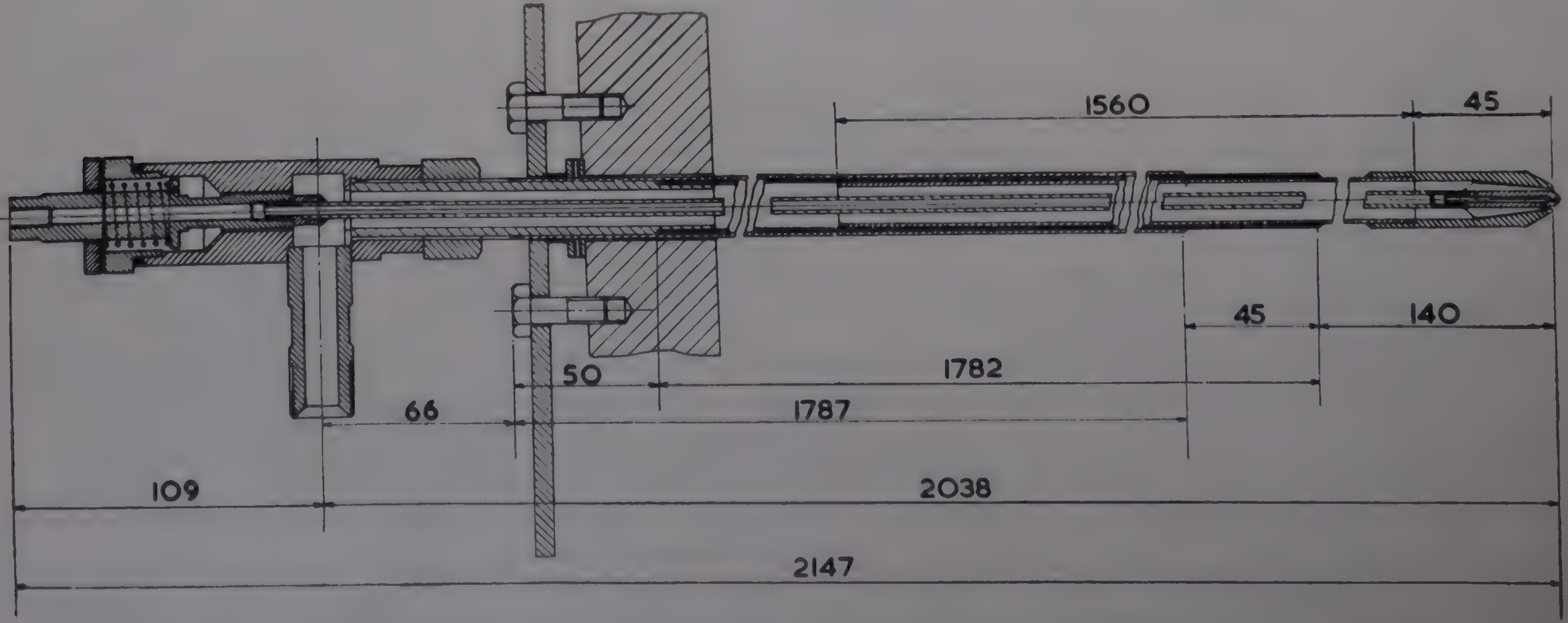
Oxygen line for continuous enrichment of air blast for iron smelting in the Low Shaft Furnace Pilot Plant of the National Metallurgical Laboratory has been completed. Oxygen enrichment of air blast will provide for less of heat consequent on the injection of light naphtha through the tuyere into the hearth zone of the Low Shaft Furnace Pilot Plant of National Metallurgical Laboratory. It may be appreciated that oil-cum-naphtha injection including oxygen will provide unique facilities at the National Metallurgical Laboratory.

New research facilities installed at the National Metallurgical Laboratory

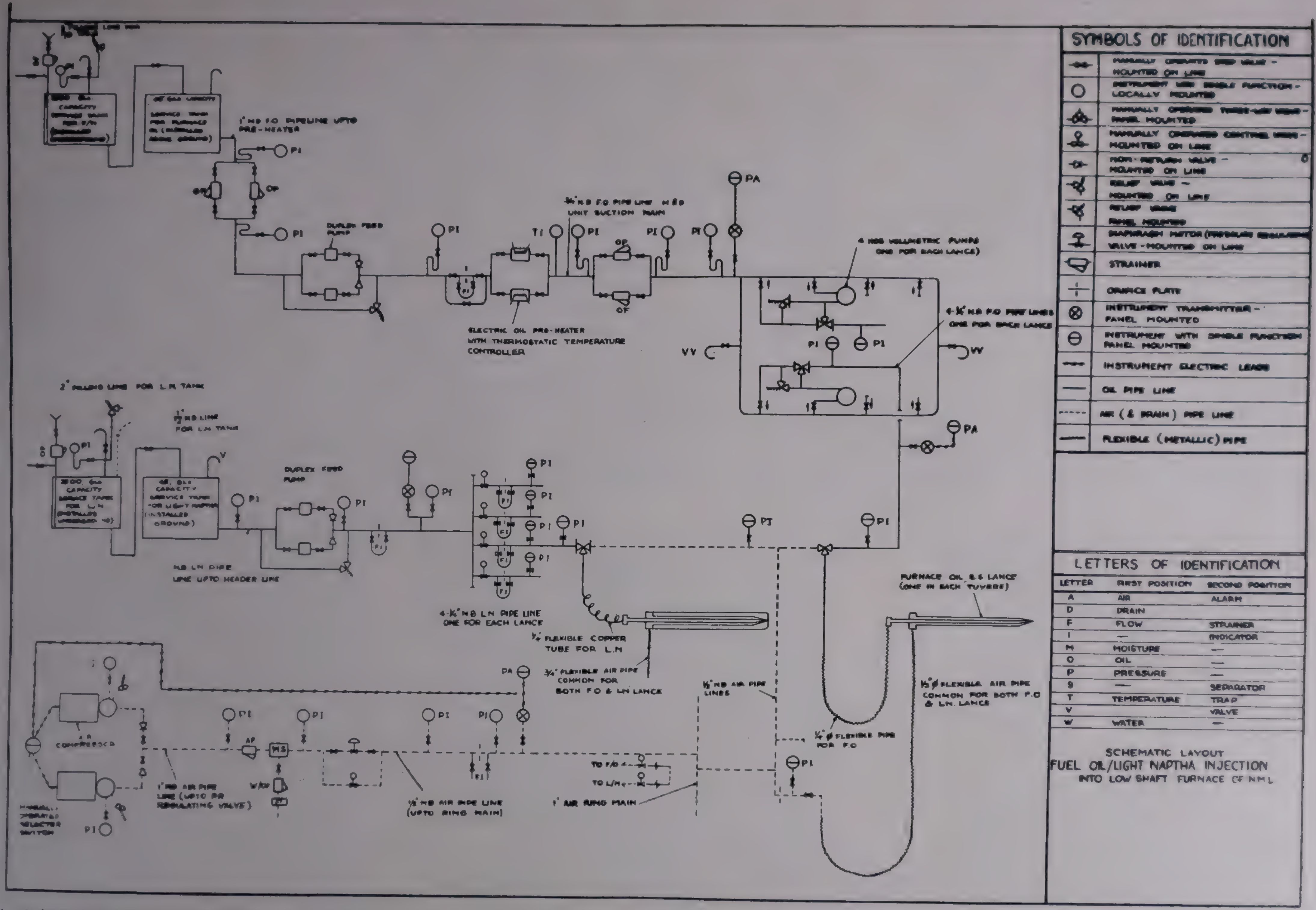
The extension work to the main building comprising the eastern, western and central wings has been completed. The new extensions provide an extra length of 160′ to the 480′ long main building of the laboratory thus providing an additional floor area of 30 000 sft. which accommodates the main new items of equipment that have been installed.

In the Main Side and Central Wings of the National Metallurgical Laboratory the following research facilities have recently been set up :

1. Vacuum metallurgy equipment containing vacuum melting and air-melting equipment on pilot plant scale.
2. Extraction Metallurgy including silico-thermal reduction of dolomite to magnesium ; hydro-metallurgy including leaching of ores, secondary refining of metals such as zinc dross, skimming residue, etc.
3. X-ray diffraction equipment and a small workshop.
4. Radio-active isotope laboratory.
5. Phase transformation studies in refractory materials in slag system.
6. Utilisation of metallugrical wastes including blast furnace and steel melting slags and their optimum utilisation for a multitude a uses.
7. Study of non-metallic inclusions.
8. Plastic coatings of steel.
9. Electronic instrumentation, repair and fabrication.
10. X-ray fluorescence spectrometer ; mineralogical and petrological studies on ores and minerals.
11. Mechanical testing of metallurgical equipment including the vibro-phore pulsator.



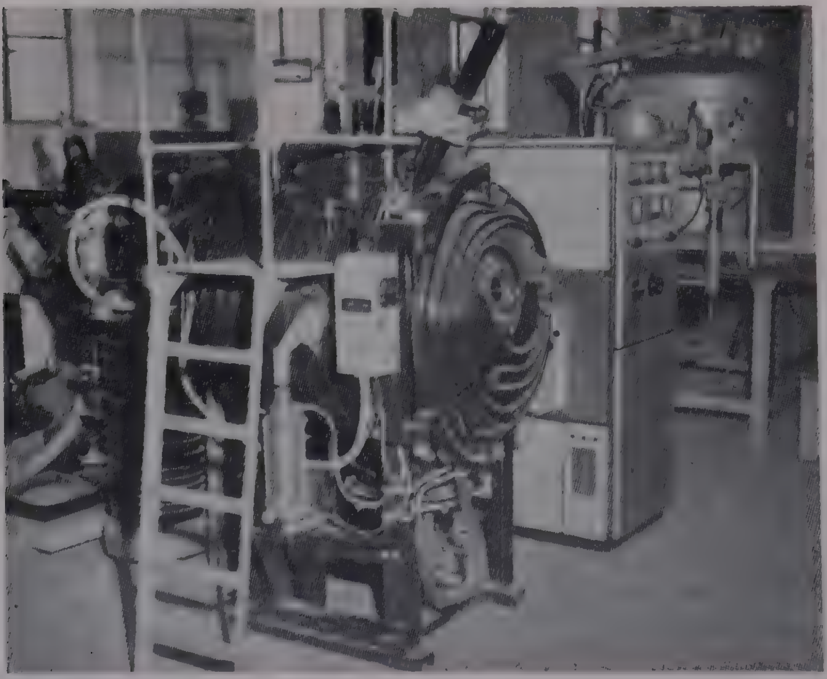
3 *Lance assembly for the injection of light naphtha into the Low Shaft Furnace Pilot Plant of the NML.*


1" N.B. F.O. PIPELINE UPTO PRE-HEATER
DUPLEX FEED PUMP
ELECTRIC OIL PRE-HEATER WITH THERMOSTATIC TEMPERATURE CONTROLLER
3/4" N.B. F.O. PIPE LINE N.B. UNIT SUCTION MAIN
4 NOS VOLUMETRIC PUMPS ONE FOR EACH LANCE)
4-1/2" N.B. F.O. PIPE LINES ONE FOR EACH LANCE
PI
PA
TI
PT
VV
OF
2" FILLING LINE FOR L.N. TANK
1/2" NB LINE FOR L.N. TANK
CAPACITY SERVICE TANK FOR L.N. (INSTALLED UNDERGROUND)
45 GLS CAPACITY SERVICE TANK FOR LIGHT NAPTHA (INSTALLED GROUND)
NB LN PIPE LINE UPTO HEADER LINE
DUPLEX FEED PUMP
4-1/2" N.B. L.N. PIPE LINE ONE FOR EACH LANCE
1/4" FLEXIBLE COPPER TUBE FOR L.N.
3/4" FLEXIBLE AIR PIPE COMMON FOR BOTH F.O. & L.N. LANCE
FURNACE OIL & L.S. LANCE (ONE IN EACH TUYERE)
1/2" N.B. AIR PIPE LINES
1/2" Ø FLEXIBLE AIR PIPE COMMON FOR BOTH F.O & L.N. LANCE
1/2" Ø FLEXIBLE PIPE FOR F.O
TO F/O
TO L/N
1" AIR RING MAIN
1/2" NB AIR PIPE LINE (UPTO RING MAIN)
1" NB AIR PIPE LINE (UPTO PR REGULATING VALVE)
AIR COMPRESSOR
MANUALLY OPERATED SELECTOR SWITCH
AF
MS
DA
SYMBOLS OF IDENTIFICATION
MANUALLY OPERATED STOP VALVE - MOUNTED ON LINE
INSTRUMENT WITH SINGLE FUNCTION - LOCALLY MOUNTED
MANUALLY OPERATED THREE-WAY VALVE - PANEL MOUNTED
MANUALLY OPERATED CONTROL VALVE - MOUNTED ON LINE
NON-RETURN VALVE - MOUNTED ON LINE
RELIEF VALVE - MOUNTED ON LINE
RELIEF VALVE PANEL MOUNTED
DIAPHRAGM MOTOR (PRESSURE REGULATING) VALVE - MOUNTED ON LINE
STRAINER
ORIFICE PLATE
INSTRUMENT TRANSMITTER - PANEL MOUNTED
INSTRUMENT WITH SINGLE FUNCTION PANEL MOUNTED
INSTRUMENT ELECTRIC LEADS
OIL PIPE LINE
AIR (& DRAIN) PIPE LINE
FLEXIBLE (METALLIC) PIPE
LETTERS OF IDENTIFICATION
LETTER FIRST POSITION SECOND POSITION
A AIR ALARM
D DRAIN
F FLOW STRAINER
I — INDICATOR
M MOISTURE —
O OIL —
P PRESSURE —
S — SEPARATOR
T TEMPERATURE TRAP
V VALVE
W WATER —
SCHEMATIC LAYOUT
FUEL OIL/LIGHT NAPTHA INJECTION
INTO LOW SHAFT FURNACE OF NML

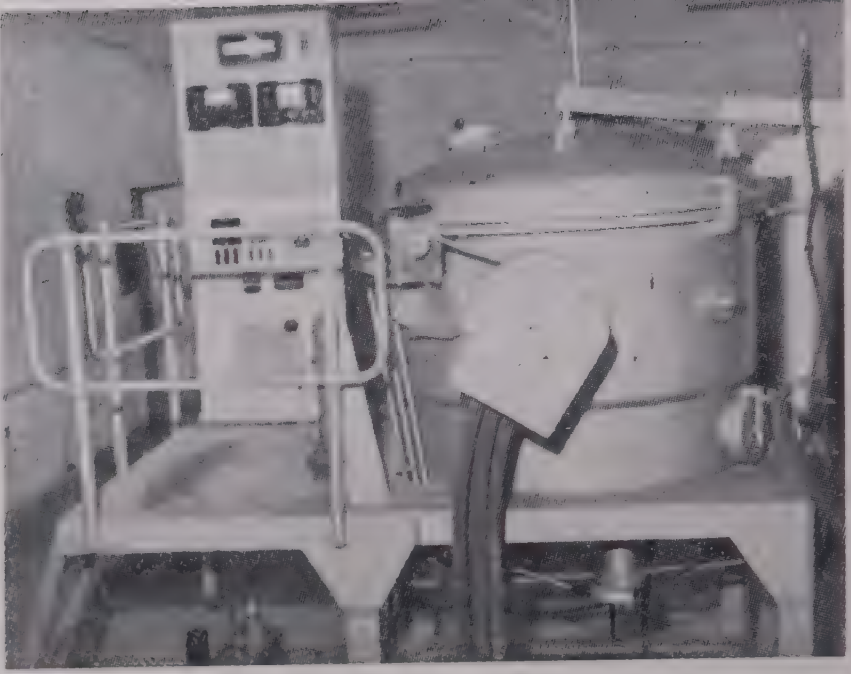
4 *Schematic layout of fuel oil/light petroleum Naptha injection into Low Shaft Furnace of the National Metallurgical Laboratory.*

5 *Extensions to the central wing of the National Metallurgical Laboratory housing the library, auditorium, liaison, information, operational research and design Engineering secions.*

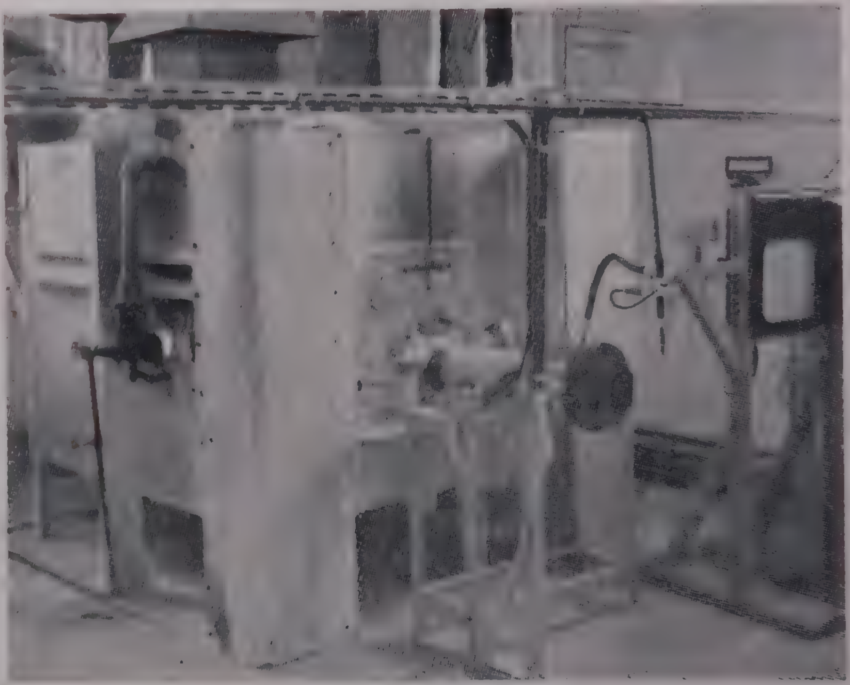
6 *A view of the extended western wing of the National Metallurgical Laboratory, connected to the pilot plant Bay of the laboratory.*



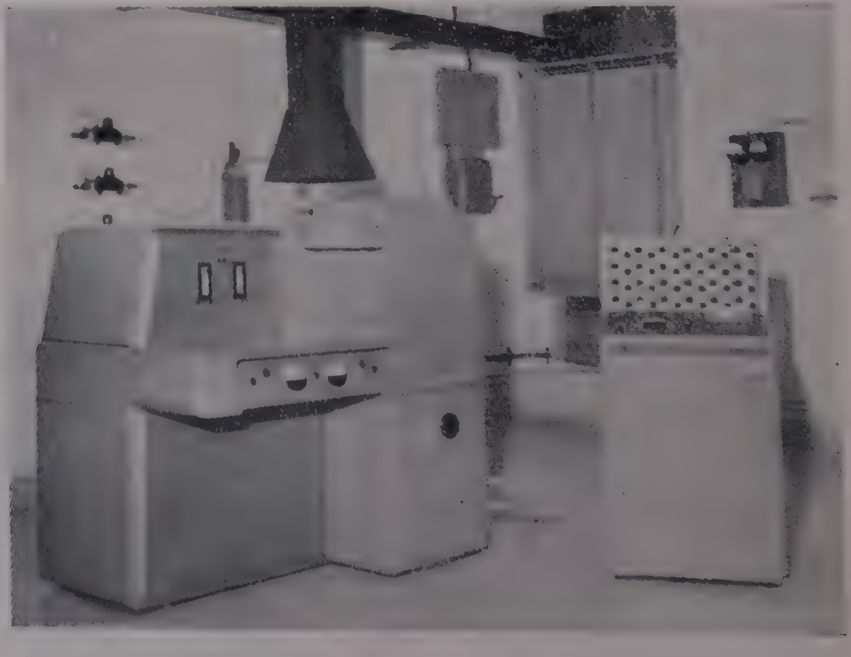
7 *60 lb VIA-VAC Vacuum induction melting and casting furnace.*



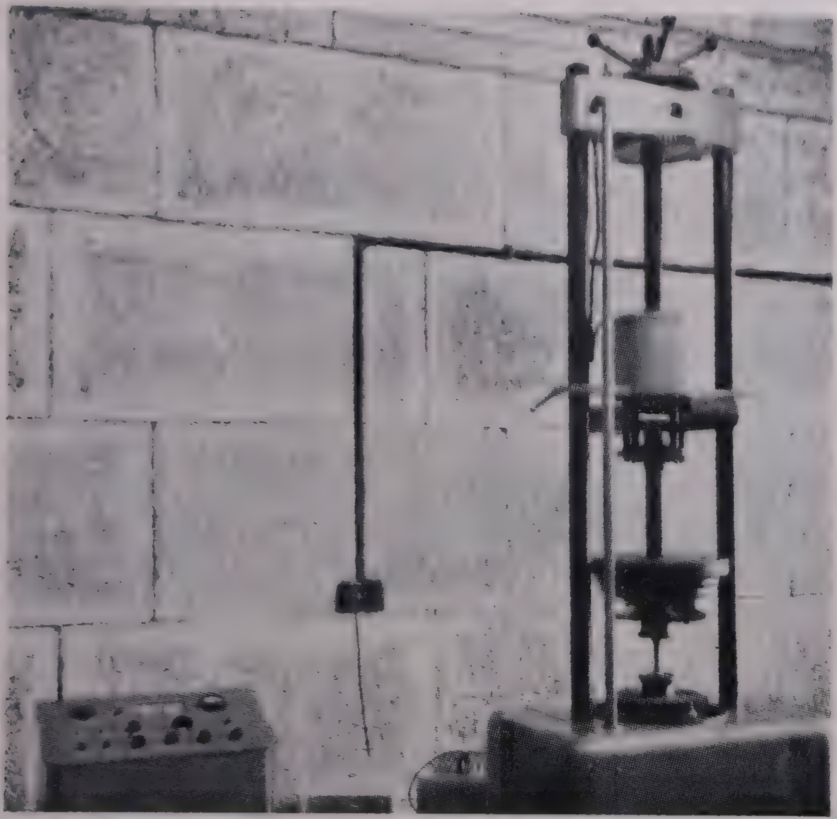
8 *The 28 lb Edward's vacuum induction melting and casting furnace*



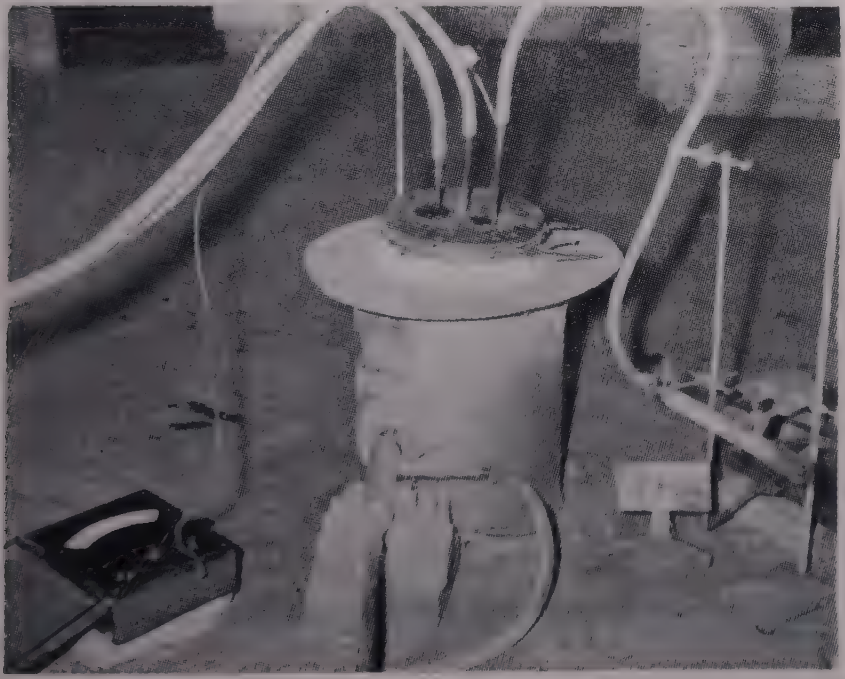
9 *The 25 lb/day Magnesium Pilot Plant designed and fabricated at the National Metallurgical Laboratory.*



10 *'Norelco' Autrometer for X-ray fluoresence analysis installed at the National Metallurgical Laboratory.*



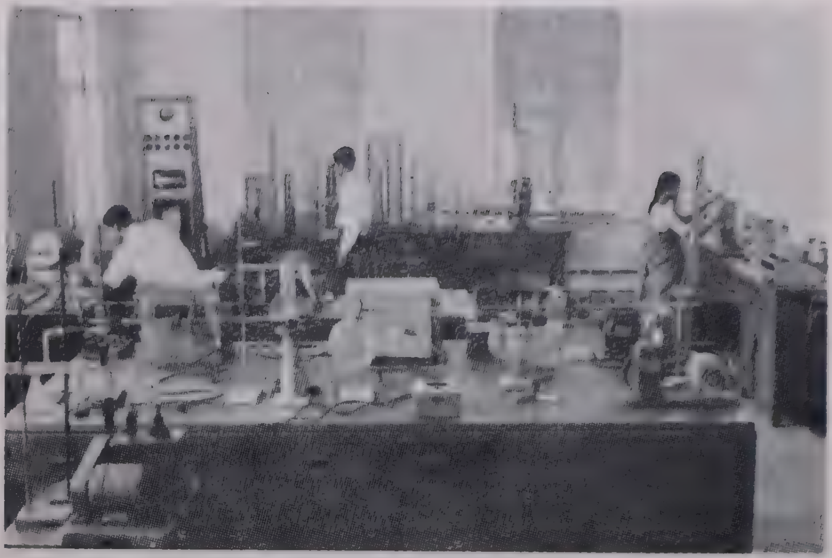
11 *High-frequency, vibrophore installed at the National Metallurgical Laboratory for studying fatigue properties of metals at room and high temperatures.*



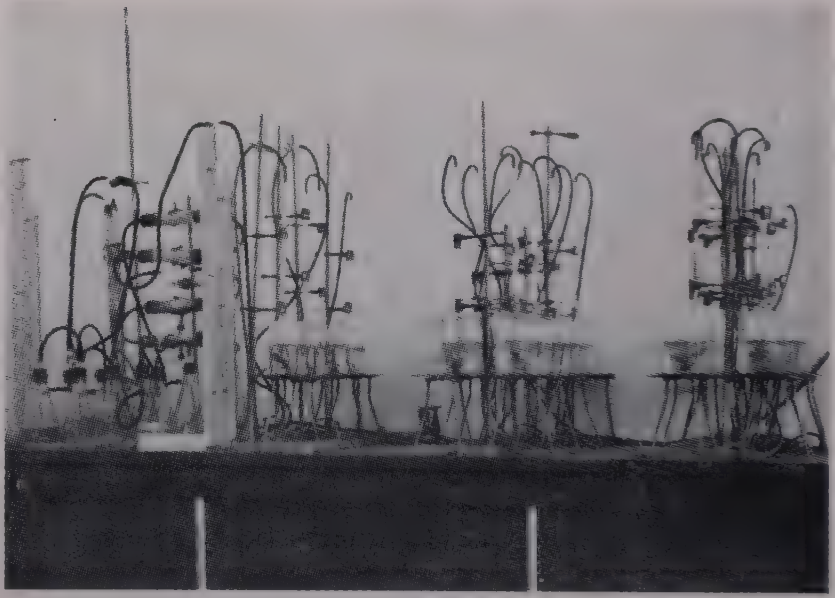
12 *Vacuum distillation unit for zinc recovery.*

12. Differential thermal analytical equipment for fundamental studies into slags and minerals.
13. Precision workshop.
14. Alloy Steel division.
15. Extractive metallurgy research division including non-ferrous metallurgy.
16. Iron and Steel research division.

The Central wing contains the library block, auditorium and liaison, information and operational research facilities. Additionally a full-fledged design engineering section is operating on the top floor of the Central wing engaged in original design engineering and provision of working drawing for the fabrication of the Pilot plants in the NML workshop and industrial projects.

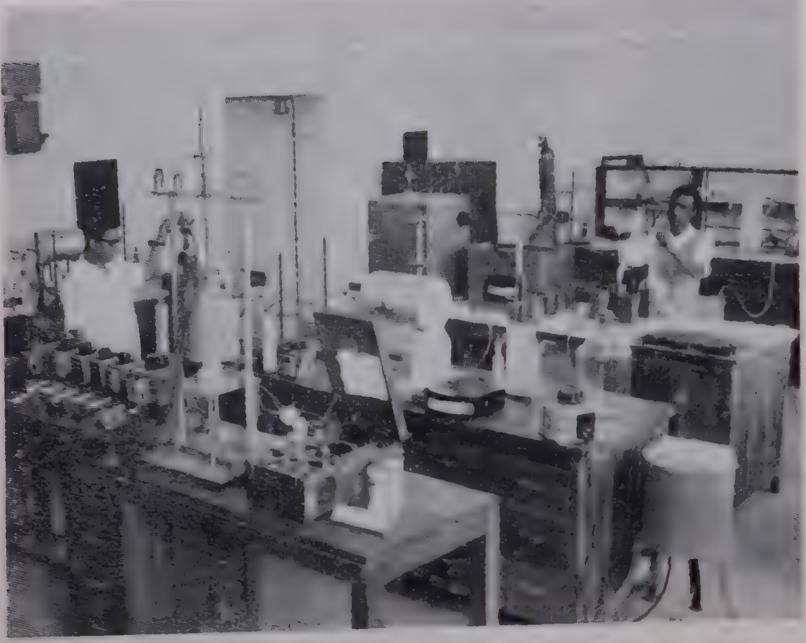


13 *A view of the Extractive Metallurgy Division including research facilities for non-ferrous metallurgy at the National Metallurgical Laboratory.*



14 *A view of the setup for the study of impingement corrosion resistance of various non-ferrous alloys.*

15 *The corrosion laboratory.*



16 *The Iron and Steel research division of the National Metallurgical Laboratory.*

17 *Physical metallurgy research facilities provided at the National Metallurgical Laboratory.*

18 *Design engineering section of the National Metallurgical Laboratory.*

The value of the equipment housed in these side and central wings is of the order of over Rs 1·5 million. The wings have been built up at a cost of rupees 1·2 million and constitute a double-storied structure.

The new extensions were declared open by Mr M. C. Chagla, Union Minister for Education, Government of India, and the napthha injection trials were inaugurated by Prof. Humayun Kabir, Union Minister for Petroleum and Chemicals, Government of India, on 6th February, 1965. The Union Ministers in their inaugural speeches greatly commended the highly valuable work done by the National Metallurgical Laboratory in diverse fields and complimented Dr B. R. Nijhawan, Director, National Metallurgical Laboratory and his team of workers on their dedicated work. Sir Jehangir Ghandy, Chairman, Executive Council of National Metallurgical Laboratory, who presided over the function paid his sincere tributes to Dr Nijhawan, Director, National Metallurgical Laboratory and his colleagues for their single minded devotion and the excellent work they were doing in the field of minerals and metals industry of the country under the tempo of successive Five Year Plans of the country.

LIST OF DELEGATES ATTENDING THE SYMPOSIUM ON MICRO-METALLURGY

DELEGATES FROM OVERSEAS

1. Capus, Dr J.M.,
   Gillette Industries Ltd, Research Laboratories, England.
2. Craik, Dr R. L.,
   Head of Laboratories, Metallurgy Division, British Iron and Steel Research Association, Sheffield, England.

3. Friesen, N.,
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4. Harrison, J. L.,
   Manager, Iron and Steel Processes, British Oxygen Co. Ltd, Hammersmith House, London.
5. Imai, Dr Y.,
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6. Mal, Dr M. K.,
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7. Miller, J. R.,
   Special Technical Adviser, Centre for Industrial Development, United Nations, New York.

8. Safoglu, Dr A.,
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9. Saito, T.,
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10. Scott, Douglas.,
    National Engineering Laboratory, Department of Scientific and Industrial Research, Glasgow, England.

11. Tanino, M.,
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17. Anjaneyulu, T.S.R.,
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19. Banerjee, A.,
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20. Banerjee, A.K.,
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31. Chatterjee, Dr D. P.,
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32. Chatterjee, Dr G. P.,
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38. Das, N. C.,
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40. De S. K.,
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    Actg Head, Department of Metallurgy, Banaras Hindu University, Varanasi.
43. Dhanbhoora, Dr D. R.,
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44. Engineer, B. B.,
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    Smelter Superintendent, Indian Copper Corporation Ltd, Ghatsila.

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Partner, General Metallurgical Company, Jamshedpur.
73. Paranjpe, Dr V. G.,
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78. Prosad, Kshitishwar,
Chairman, Foundry Pig Iron Panel (Constitued by Govt. of India), Howrah.
79. Punj, R. P.,
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81. Rao, K. N. P.,
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82. Rao, Lt. Cdr. V. N. Madhav,
Defence Metallurgical Research Laboratory, Hyderabad.
83. Rao, M. S.,
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90. Saha, P. G.,
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94. Shankar, M. B.,
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95. Sharma, D. N.,
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104. Vaswani, Arjan,
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105. Venkateswarlu, G.,
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106. Visvanathan, S.,
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107. Wadia, N. J.,
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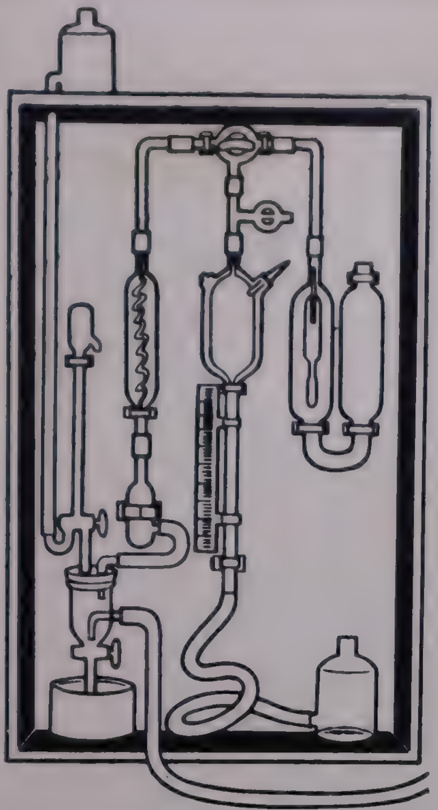

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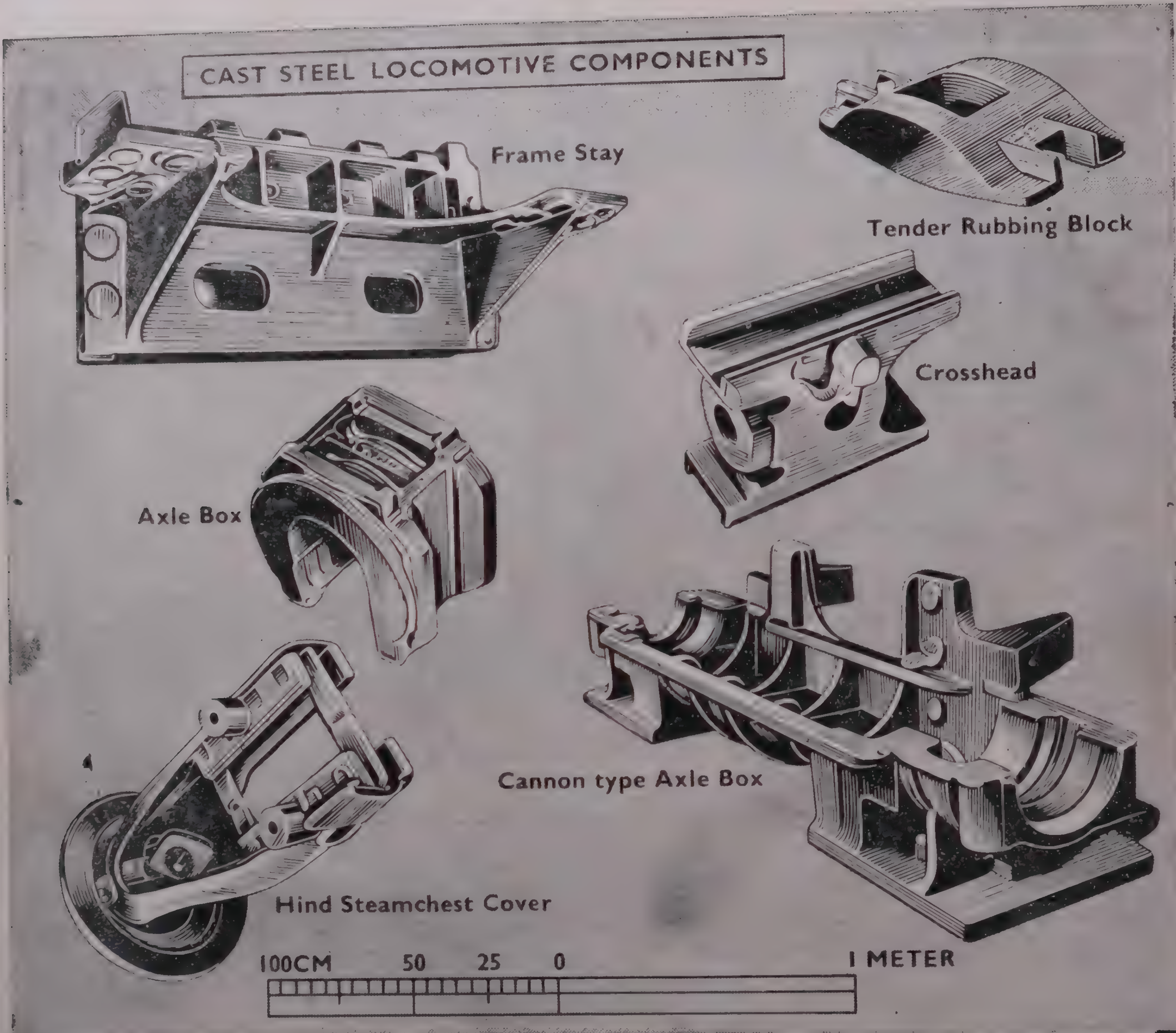
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VOLUME VII **NUMBER 2** **MAY 1965**

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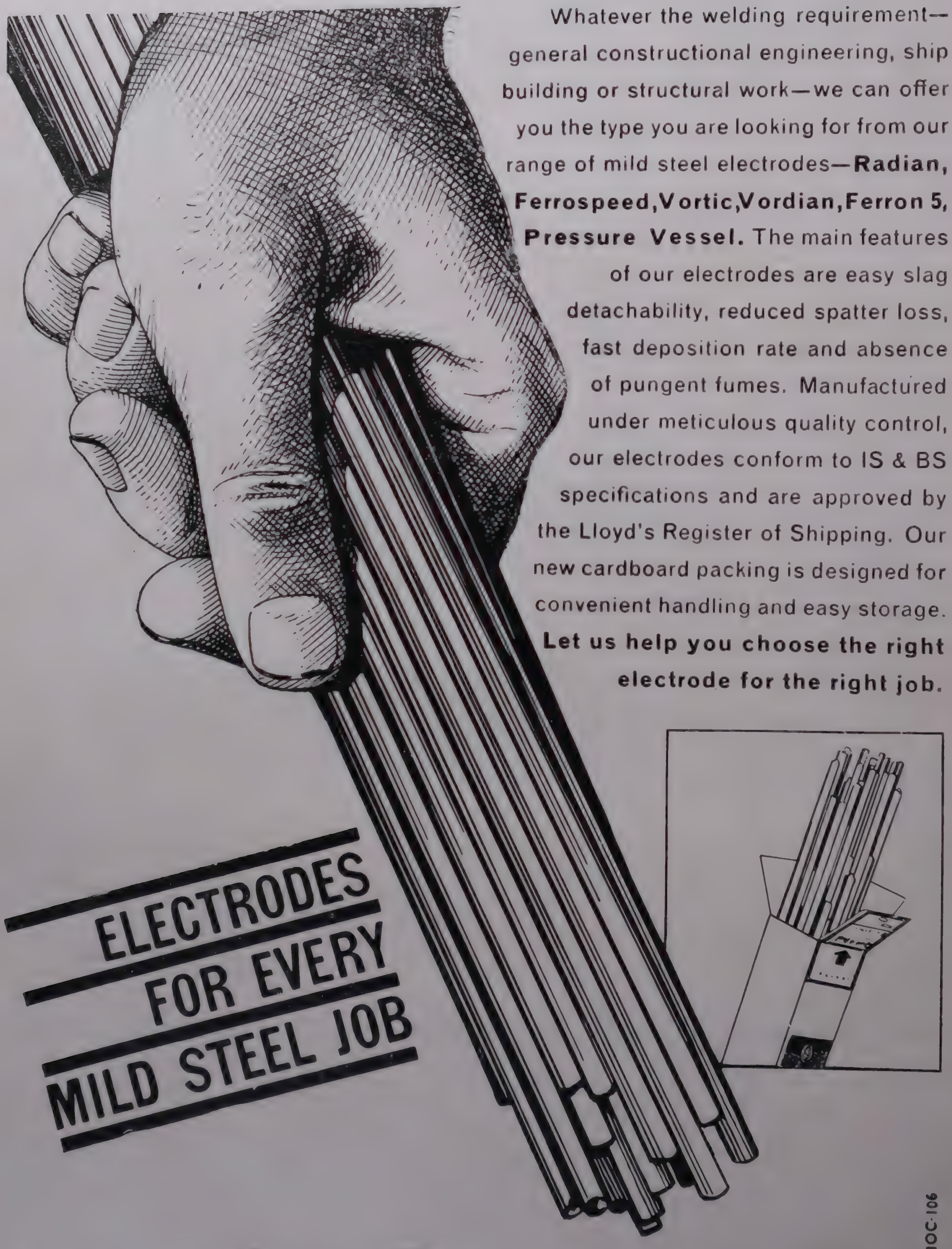

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NML TECHNICAL JOURNAL

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Micro-Metallurgy

AMONGST the divers facets of fundamental research and equally dispersed themes of applied research in metallurgical fields, the subject of 'Micro-Metallurgy' perhaps provides the 'missing link'—missing in the sense that it has relatively escaped the metallurgical limelight, even though unobtrusively providing the 'link' between theory and the practice in the growth of a vast array of specialized ferrous and non-ferrous alloys in current usage.

The major effects upon metals and their alloys of minute changes in their composition both additive and the reverse in terms of serious damage or of equal metallurgical benefit, have provided the basis for some major fundamental research studies besides providing the pattern for the 'applied' development of multitude alloys of inestimable value to the growth of modern engineering industries in this jet and space age. The mechanism of how so much is conferred by the so minute and the recurring explanations, theories and hypotheses, present to theoretical scientists and practical metallurgists a fascinating metallurgical spectrum of endless research activity and applied development work. At the National Metallurgical Laboratory, research and development themes to study the role of minute additions to ferrous and non-ferrous metals for the production of diverse ranges of alloys to exacting specifications and needs represent a major field of the laboratory's research activities. In this context, the Symposium on 'Micro-Metallurgy' recently organized by the National Metallurgical Laboratory was opportune and well attended by delegates from home and many overseas distinguished scientists and metallurgists.

Twentynine technical papers covering diverse aspects of Micro-Metallurgy were presented and discussed during the four-day NML Symposium held during end of March, 1965.

In this issue of the NML Technical Journal, a review of the NML Symposium proceedings has been given. The Symposium proceedings will shortly be published containing the technical papers presented and the discussions during the memorable NML Symposium week in the warm Indian weather punctuated by heavy rain showers to show our overseas delegates that India is not such a hot country after all.

Symposium on 'Micro-Metallurgy—The Role of Minute Additions to Ferrous and Non-Ferrous Metals and Alloys'—A Review

P. K. Gupta

MICRO-METALLURGY relating to the role of minute additions to metals and alloys presents a fascinating metallurgical spectrum ranging rom basic and fundamental research studies to applied esearch themes covering the development of alloys and uper alloys dependent chiefly for their metallurgical haracteristics and physical properties on minute additions of certain elements. The subject of micro-metalurgy, however, is not new. Illustrations of minute dditions exercising major damaging effects whilst thers conferring equally beneficial properties in the ast and almost unlimited series of ferrous and nonerrous alloys are abundant: yet the mechanism of ow so much is conferred by the so small and the ecurring explanations, hypotheses, theories, etc. thereof resent to the theoretical scientist and practical metalurgists scope for ceaseless research activity and deveopment applied work. The vast technical literature on he subject, though rich in its technical wealth, presents wide array of loosely dispersed and scattered technial references in manuals, text books and scientific and echnical journals.

With a view to focus attention on a multitude of spects of micro-metallurgy, a Symposium on 'Micro-Metallurgy' was organized by the National Metallurgical Laboratory from 29th March to 1st April, 1965, so as o provide an international forum to discuss the role f minute additions to ferrous and non-ferrous metals nd alloys and to exchange technical 'know-how', xamine inter-related problems and facilitate further esearch studies on the subject.

The Symposium drew a large gathering and more han 200 delegates from all over the world including op ranking scientists and technologists participated in ts deliberations.

The Symposium was inaugurated by Shri Asoka Mehta, Deputy Chairman, Planning Commission; Sir ehangir Ghandy, Chairman, Executive Council, National Metallurgical Laboratory, presided at the function.

Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, in welcoming the distinguished delegates from India and abroad, said that such international Symposia offer stimulation of thought and provide an ideal forum for exchange of technical 'know-how' and 'know-why' of diverse aspects of the subject.

Continuing, Dr Nijhawan said that the subject of Symposium is somewhat unusual e.g. 'Micro-metallurgy —The Role of Minute Additions to ferrous and non-ferrous metals and alloys' which bridges across the work of fundamental research studies and that of applied research development themes. During the successive Five Year Plans, the National Metallurgical Laboratory is called upon to handle various research and development projects essential to the growth of mineral and metallurgical industries, challenging in their objectives and the challenge is being effectively met. A main theme of activity at the National Metallurgical Laboratory is educational, such as the organisation of Symposia on metallurgical subjects of topical interest like the present one. Research and development studies undertaken so far at the National Metallurgical Laboratory have been effectively rewarding whilst the research and research on how so much is contributed by the so small, will be ceaseless and practically unending, in the planning and execution of which, the National Metallurgical Laboratory is actively engaged upon.

Sir Jehangir Ghandy, Chairman, Executive Council of the National Metallurgical Laboratory stated that the National Metallurgical Laboratory has been holding an international Symposium every year on subjects of fundamental and applied metallurgical interests and this is the 14th Annual Symposium to be organized under its auspices. The National Metallurgical Laboratory is now playing a progressive role in the growth and development of mineral and metallurgical industries in the country and it has been acknowledged as 'deservedly occupying a high metallurgical reputation internationally'.

Sir Jehangir Ghandy said that the National Metallurgical Laboratory has undertaken very valuable research work on various aspects of micro-metallurgy. These related to grain-size control in steel, abnormality

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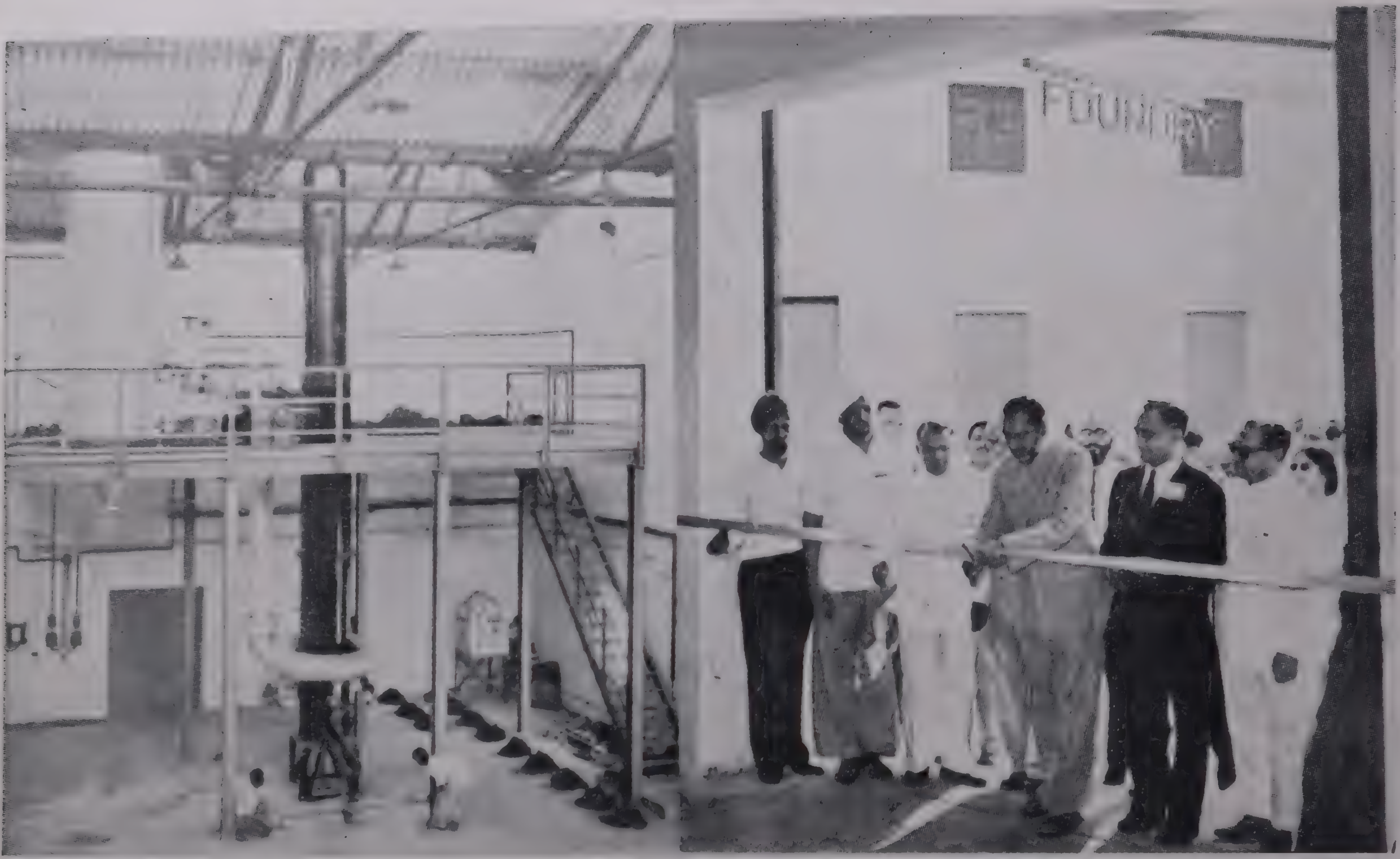
Mr P. K. Gupta, Scientist, National Metallurgical Laboratory.

Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, welcoming the delegates on the inaugural day of the Symposium.

and strain-ageing effects in steel. Research is also being conducted on micro-additions of rare-earth elements to stainless steels and aluminium-magnesium alloys, and on the ageing of aluminium alloys. In addition, studies on phase changes in relation to micro-constituents, micro-metallurgy of aluminium-silicon alloys and heat-resistant alloys and analytical techniques for measuring are being made. The subject of micro-metallurgy is vast and requires cataloguing of hypotheses and defining those needing attention to research facilities and equipment available for specialised research techniques. Sir Jehangir extended on behalf of the Executive Council of the National Metallurgical Laboratory, their sincere thanks and deep appreciation to Dr B. R. Nijhawan, Director, National Metallurgical Laboratory and his colleagues for the valuable research and development work being done by them and also for the fully adequate arrangements made for the Symposium.

Shri Asoka Mehta, Deputy Chairman, Planning Commission, while inaugurating the Symposium said that the subject of the Symposium is of profund interest particularly to developing countries ; because the subject tries to find out how the minute additions have far reaching consequences on the properties of metals and alloys. Thus it becomes possible for a country lacking certain crucial resources to make up by this kind of micro-marginal efforts and devices. Then again because a minute particle may have far reaching consequences, it becomes possible to cut down the cost structure. Continuing Shri Mehta said, what is liked about this particular laboratory is that it has succeeded in assembling together a group of men and women, young scientists, young engineers, who have confidence, ability, ingenuity and improvisation. These are essential qualities that are needed today and in the next few years. Nothing must be allowed to intimidate. There will be difficulties and if difficulties are going to intimidate then this one-seventh of world's humanity will remain always, a load, a burden for the rest of the world to carry. But if there is confidence, ingenuity, willingness to put in whatever intellectual and physical efforts that are to be put in and above all improvise, there is no reason that in the next 10 years the country should not be able to move forward in the manner where it can play its part in the concert of the world whatever be the symphony that the concert may be played at the particular time. Shri Mehta stated that it is the responsibility of the Planning Commission as the central highest thinking organisation set up by the Government to go out and find out and make it possible for all these creative elements in the country to come together and make their critical and decisive contributions. Concluding, Shri Asoka Mehta congratulated Dr Nijhawan and his colleagues in organising the International Symposia and on their splendid work in verdise fields.

Dr Husain Zaheer, Director-General, Scientific and Industrial Research, addressing the Delegates to the Symposium on 'Micro-Metallurgy' complimented the National Metallurgical Laboratory for the valuable work done on diverse fields and the number of project-oriented industrial problems undertaken on behalf of the industries. In this connection, he referred to the tribute paid



Shri Asoka Mehta, Deputy Chairman, Planning Commission, opening the New Foundry Block of the National Metallurgical Laboratory.

to the National Metallurgical Laboratory by the Third Reviewing Committee headed by Shri A. Ramaswamy Mudaliar that the National Metallurgical research work, has forged close links and won the confidence of the Indian mineral and metallurgical industries. The valuable suggestions given by the Reviewing Committee that the National Metallurgical Laboratory should also focus attention on fundamental aspects of the work has also been implemented immediately by the holding of this Symposium on Mirco-Metallurgy in which field this Laboratory has done pioneering work on the fundamental aspects of minute additions to metals and alloys. As far as the National Metallurgical Laboratory is concerned, Dr Zaheer said, "It has been fortunate to have such a young and dynamic Director, in the person of Dr B. R. Nijhawan, who has done much in bringing this Laboratory to the international forefront and status." He expressed his sincere hope that this Laboratory will provide the most needed solutions to the multifarious problems faced by the industry in the mineral metallurgical fields with its vast net-work of pilot plant and the well-talented research staff working under the able leadership of Dr B. R. Nijhawan. He also paid a tribute to Mr Asoka Mehta, Deputy Chairman, Planning Commission, for this depth of vision and deep insight in the planned economy of the country and his faith in the indigenous talent in promoting the cause of scientific and industrial research.

Shri M. S. Rao, Chairman, Hindustan Steel Limited, who was the Chief Guest, referred to the great service that the National Metallurgical Laboratory rendered to Hindustan Steel Ltd. not merely on the basis of general research studies carried out but because, the Laboratory had carried out pilot plant studies specifically for Hindustan Steel Ltd. on beneficiation of the iron ores which go to supply the three Steel Plants of Hindustan Steel Ltd. and also studies on sintering of the Barsua iron ore for Rourkela and the Rajhara iron ore for Bhilai Steel Plant. The Natioal Metallurgical Laboratory is regarded as the main research centre for original studies for Hindustan Steel Ltd. Continuing, Shri Rao said, The subject-matter of the Symposium is perhaps as entrancing in the vistas which it opens, as the study of the tiny atom has been in nuclear physics; and perhaps even as the study of the atom has placed in man's hand enormous energy, power and speed, so also purposive research of the micro-constituents in metals and alloys would put in our hands not only the ability to control or eliminate their occurrence so as to improve the speed and quality of production of the metals and alloys with reference to the raw materials available in our country; but, in course of time, it should be possible, in the making of alloy steels in our country to replace by some indigenous elements certain rare and costly elements not readily available in our own country. The prospect of developing new and better alloys is also great."

Technical sessions

Twenty-nine technical papers covering various facets of micro-metallurgy were presented and discussed in six technical sessions.

The first technical session opened with five technical papers in the morning followed by four in the afternoon.

Group photograph of some of the delegates to the Symposium.

Dr R. L. Craik, Head of BISRA Laboratories, England presented laboratory trials data relating to low carbon, high manganese, niobium and vanadium steels in both the controlled rolled and normalised conditions. Low carbon contents in ferrite-pearlite steels proved to be beneficial to toughness and weldability. However, in air-cooled carbon steels, low carbon contents led to coarse ferritic grain structures which are detrimental to yield strength and toughness properties. Manganese lowers the transformation temperature and is beneficial to toughness in moderate amounts. Niobium and vanadium are excellent grain refining additions. Dr J. M. Capus of Gillette Industries, England, studied the influence of residual trace elements on the mechanical properties of constructional alloy steels. The deleterious effect of minor residual elements limits the development of alloy steels particularly for high strength applications; their weldability is also affected. In many high performance constructions, the usefulness of alloy steels is limited by the properties which can be obtained after welding. It is, therefore, imperative to concentrate attention on weldability problems of high tensile steels for example, since in many new applications, e.g. rocket motor casings, welding is an unavoidable step in the fabrication process.

Mr L. Nemethy, of Atlas Steels, Canada, discussed the effects of rare earth metals in stainless steel making. After the Second World War, production of stainless steels took a big step towards mass production, due to the development of numerous new applications such as automobile trims, cooking utensils, architectural applications and food processing equipment. A number of special austenitic stainless grades were developed for special applications, such as the extra low carbon austenitic grades, molybdenum bearing stainless steels, special austenitic steels for cold heading and welding wire applications, etc.

Despite the many improvements, the processing of stainless steels presented some difficulties particularly during the initial stage of hot working and the author critically discussed the effect of rare earth metals addition to solve the problem of hot workability.

Techniques for the study of micro-phases and their influence on material properties were studied in details by Mr D. Scott, Head Metallurgy Section, National Engineering Laboratory, Department of Scientific and Industrial Research, England. In the National Engineering Laboratory many metallographic techniques are currently in use in materials research including electron, microscopy, replica methods, thin foil technique fractography, dynamic electron metallography, etc. Messrs B. F. Oliver, F. Garofalo, S. Arajs and R. Priestner of Edgar C. Bain Laboratory for Fundemantal Research, United States Steel Corporation, USA contributed a paper on the purification of iron by selective prefurification and oxidation zone melting, property measurements and minor impurity contents.

In the afternoon session Prof. Y. Imai of Tohoku University, Japan presented his studies on the transformation of austenite to martensite based on statistical thermodynamics and crystallography using iron-nitrogen alloys. Mr. M. Tanino of Yawata Iron and Steel Co., Japan, spoke of the effect of a small amount of vanadium and niobium on the macro structures and the strength of proeutectoid ferrite of iron carbon alloys. Mr T. Saito, Technical Research Laboratory, Kawasaki Steel Corporation, Japan dealt with the effect of minor elements on normal grain growth in singly oriented silicon iron and presented investigation data relating to the normal grain growth of cold rolled 3% silicon-iron sheet. Dr T. R. S. Goel, Delco Radio Division, USA and Dr F. H. Vitovec, University of Wisconsin, USA contributed a paper entitled "Effect of Molybdenum on the grain boundary relaxation of iron".

In the third and fourth technical sessions ten papers were presented, six in the morning and four in the afternoon.

In his leading paper on the scope of research in micro-metallurgy at the National Metallurgical Laboratory, Dr B. R. Nijhawan, Director, NML, stated that research in micro-metallurgy bridges across the work of fundamental research studies and that of applied development themes thereby providing the link between therory and practice. The subject of "Micro-Metallurgy" he added, is not new—almost a decade back, at one of the NML Symposia, the role of 'Micro-Metallurgy' in relation to alloy steels was discussed with particular reference to some pioneering work undertaken on the subject at the National Metallurgical Laboratory. Basic and applied researches on diverse facets of 'micro-metallurgy have since been pursued at the National Metallurgical Laboratory ; some of the themes have related to effects of micro-additions on grain-size control of steel and on abnormality, strain-ageing effects in steel in relation to residual micro-constituents, micro-additions of rare earths to stainless steels and aluminium magnesium alloys, micro-metallurgy of liquid metals ageing of aluminium alloys in relation to micro-constituents, micro-metallurgy of aluminium-silicon alloys and heat resistant alloys and analytical techniques for measuring micro-additions to alloys. Research studies undertaken so far have been fully rewarding whilst the search and research on, how so much is conferred by the so minute, present a fascinating metallurgical spectrum for unending research programming, in the planning and execution of which, the National Metallurgical Laboratory currently is actively engaged upon.

The subject of abnormality in steels was taken up in another paper by Dr B. R. Nijhawan, Dr A. B. Chatterjea, and Dr S. S. Bhatnagar, (NML). This subject which originated from case-carburization treatments to promote high surface hardness and came to lime-light following the presence of 'abnormal soft spots', in none-the-less important and interesting from both theoretical and practical standpoints, despite the developments of alternative modes of surface-hardening other than case-carburisation. Micro-additions of aluminium and nitrogen to steels exercise significant effects on their austentic grain growth characteristics and physical properties. Effects of such micro-additions judiciously made, in relation to the properties, isothermal transformation characteristices. MS points and grain-growth characteristics of steels have been outlined in a paper entitled 'Micro-Metallurgy of austenitic grain size control of steels' by A. B. Chatterjea and Dr B. R. Nijhawan (NML). It was established on the basis of their work that in steels containing optimum aluminium content, the precipitation of AlN provided the requisite grain-growth inhibition whilst its solution led to abnormal grain-growth. The agglomeration of AlN in high aluminium bearing steels caused the reversion to normal grain-growth behaviour.

Dr K. B. Mehta, Dy. General Manager, Foundry Forge, Heavy Engineering Corporation Ltd., Ranchi, discussed the effect of Aluminium additions on the primary grain size of steel castings. The author presented the results of his studies on the casting conditions such as the state of deoxidation of the melt, casting temperature, pouring rates and turbulence of the melt during solidification and correlated these to the as-cast primary structure in steel castings. The effects of micro-impurities and alloying elements on zirconium and zircaloy-2 were reviewed by Messrs H. C. Katiyar, P. Pande, K. B. Moorty and N. K. Rao, Atomic Energy Establishment, Trombay. Mr L. J. Balasundram and Dr Rajendra Kumar (NML) examined the distribution and function of micro-phases and micro-additions in metals and alloys and attempts on the basis of their studies to correlate the micro-additions in subtractions with the mechanical properties.

The afternoon session comprised 4 papers. Mrs B. Minari, Dr H. J. Latiere and Mr R. Michaud presented their work at the Physical Research Centre, France, on the morphology and polygonisation of copper whiskers in the from of ribbons. The importance of micro-metallurgy in non-ferrous metals and alloys used in navy was discussed at length by Mr G. Venkateswarlu, Naval Chemical and Metallurgical Laboratory, Bombay. The influence of small amounts of boron and zirconium on hot working characteristics and creep rupture properties of some vacuum melted nickle base alloys was reviewed by Lt. Cdr. V. N. Madhab Rao and Dr R. V. Tamhankar, who discussed details of experimental work work directed towards solving the perplexing problem of melt to melt variations of some of these alloys and the conclusions drawn thereof with respect to influence of boron and zirconium. Messrs K. Balaramamoorthy, H. C. Katiyar and N. K. Rao, Atomic Energy Establishment, Trombay, contributed a paper on 'Effect of micro-additions of alloying elements on, irradiation behaviour and mechanical properties of natural metallic uranium'.

On the concluding day in two technical sessions ten papers were presented. Mr Jatinder Mohan (NML) presented a study of surface tension of cast iron with additions of different elements. At the Pechiney Laboratories, France, electron microscopy and micro-diffraction techniques were applied to the study of the distribution of impurities in the alloys Be-Fe, Be-Al and Be-Si, and in several varieties of commercial beryllium. The results were presented by Messrs Croutzeilles and J. Moriceau. Dr G. P. Chatterjee, Dr B. P. Sen and Mr J. J. Bhattacharjee, Hindustan Steel Ltd., Durgapur, reviewed their investigations on micro-constituents in metals and alloys by the electron microprobe and by some specialised chemical technique aided with X-ray diffraction. Dr Ved Prakash (NML) gave a stndy of trace elements on ageing of aluminium-base alloys. Dr Y. N. Trehan, Messrs S. P. Bhadra, P. K. Gupte and Dr B. R. Nijhawan (NML) presented the results of their work on micro-additions to Al-Mg wrought alloys. Mr N. G. Banerjee (NML) gave his observations on recent methods of analysis of gases in metals and alloys and discussed the merits and demerits of conventional methods in use for determination of nitrogen and hydrogen. Mr R. D. Naidu and Miss M. Nirmala, Defence Metallurgical

Research Laboratory, Hyderabad, described a spectroscopic method of determination of micro amounts of elements in steels and Messrs M. K. Ghosh, P. C. Debnath, Miss Sumitra Dasgupta and Dr B. C. Kar (NML) presented method and for the spectrographic analysis of micro-constituents in ferrous and non-ferrous metals and alloys based on some new techniques developed at the National Metallurgical Laboratory. Messrs P. Koteswara Rao, S. L. N. Acharyulu and M. K. Joshi, Defence Metallurgical Research Laboratory, Hyderabad, reviewed the analytical methods in micro-metallurgy including special methods such as micro and ultramicro-techniques.

Giving a resume of the Symposium at the end of the technical sessions, Dr B. R. Nijhawan, Director of the National Metallurgical Laboratory, said that the papers submitted covered multitude aspects of the subject of micro-metallurgy which represent a vast and challenging field. Dr Nijhawan thanked all the participating delegates from various parts of the country and abroad for taking part in the deliberation of the Symposium, and expressed his appreciation of the valuable contributions on various technical points of importance which arose during the discussions. Research studies in micro-metallurgy undertaken at the NML so far have been fully rewarding, he added, and this Symposium has played its part in providing an international forum to the Metallurgists and scientists to discuss their views and exchange ideas.

The delegates were conducted round the various research divisions of the National Metallurgical Laboratory, the Low Shaft Furnace Pilot Plant, the Mineral Beneficiation Pilot Plant and other Pilot Plants of the Laboratory during the Symposium.

Consideration of Surface Area and Crystallinity of Kaolinite as Factors in its Base Exchange Capacity

P. Prabhakaram

With a view to study the influence of surface area and crystallinity of kaolinite on its 'bec', the base exchange capacities of three kaolinitic clays were compared with their surface areas as determined by low temperature argon adsorption and crystallinity as indicated by their X-ray diffractograms in the region 16°-43° 2θ using $C\mu K_{\alpha}$ radiation coupled with their differential thermal curves. The results indicate that even though there is correlation between 'bec' and crystallinity of kaolinite in the different clays, no relation is observed between surface area and 'bec' of the different clays. It is considered that correlation may exist with surface area and base exchange due to broken bonds within the same clay but it may not hold with different clays due to some changes in the mineralogical composition and presence of minerals like tubular halloysite which can permit argon entry within the tubes and contribute to internal surface area also.

IT was shown by a number of workers[1, 2, 3] that the base exchange of kaolinite increases with increase in surface area and it is attributed to increase in the broken bonds at the crystal edges with decrease in particle size. Grim[4] pointed out that lattice distortions also will tend to increase broken bonds and hence the exchange capacity will be expected to increase as crystallinity decreases. In the present investigation also correlation could be found between crystallinity and 'bec' of kaolinite in the three clays studied but no relation could be found between surface area and 'bec'.

Materials

Clay fractions finer than 300 mesh B.S.S. of two china clays of Indian origin (Travancore and Rajmahal) and a fraction finer than 2μ of a ball clay from Rajasthan, were taken up for study. The chemical analyses of the materials and their mineralogical composition as calculated by normal method are given in Tables I and II respectively.

Experimental

The 'bec' of the clays were determined by titration of the H-forms of the clays with decinormal sodium hydroxide potentiometrically. The H-clays were prepared by contact exchange of the clays with Ambertite IR-120 (H).

X-ray diffractograms were taken with Phillips X-ray diffractometer PW-1010, using $C\mu K_{\alpha}$ radiation. The samples were prepared for analysis according to the mehtod advocated in diffractometer procedures. Differential thermal analysis was carried out using platinum foil cup containers and a vertical platinum wound tubular furnace. Calcined alumina was used as inert and a heating rate of 10°C/min. was maintained. Temperatures are expressed with reference to inert.

Surface area measurements were made by low temperature adsorption of argon according to B.E.T. method and also by adsorption of stearic acid from methanol and finding out the change in concentration of stearic acid after adsorption by titration with carbonate free NaOH conductometrically.

In stearic acid adsorption experiments, about 2 gm of the dried clay sample was weighed accurately and transferred to a 250 cc iodine flask and 100 cc of approximately 0·04 omlar solution of stearic acid in methanol was added. The contents were agitated on a mechanical shaker for 2 hours and were allowed to settle. An aliquot of 10 cc from the clear supernetant liquid was taken into a conductivity cell and additional quantity of pure methanol was added so as to permit the electrode assembly to dip into the solution. Double distilled water was added such that it forms about 10 per cent of the total volume and the resistance of the solution was measured after successive additions of carbonate free NaOH. The solution was mechanically agitated after each addition of alkali. An audiotester (Marconi type) 894 A, turned to 1000 cycles frequency was used and the resistance was measured with a Phillips multiple resistance bridge, The electrodes are of Phillips make (PR-9510) and are of the dip type. The initial concentration of stearic acid was determined in a similar way.

TABLE I Chemical analyses of the clays

Constituent per cent	Travancore china clay —300 B.S.S.	Rajmahal china clay —300 B.S.S	Ball clay<2μ
Loss at 110°C	0·28	1·12	1·86
Loss on ignition (exclusive moisture)	14·22	13·72	11·84
Total SiO_2	45·44	45·96	45·62
Al_2O_3	38·87	36·2	36·46
Fe_2O_3	1·12	0·58	0·74
TiO_2	Trace	Trace	1·96
CaO	0·4	0·64	1·42
MgO	0·11	Trace	0·64
Na_2O	Trace	0·87	Trace
K_2O	Trace	0·50	Trace

Dr P. Prabhakaram, Scientist, National Metallurgical Laboratory, Jamshedpur.

TABLE II Mineralogical composition of the clays

Sample	Muscovite %	Albite per cent	Anorthite %	Kaolinite %	Gibbsite %	Quartz %	illemenite %	Anatase %	Limonite %	Serpentine %	Moisture %
Travancore china clay —300 B.S.S.	—	—	1·9	95·4	0·6	—	—	—	1·2	0·2	0·6
Rajmahal china clay —300 B.S.S.	3·7	6·8	2·8	80 9	—	2·9	—	—	0·6	—	2·4
Ball clay $<2\mu$	—	—	6·9	85·0	—	1·6	1·5	1·2	—	2·4	1·44

Muscovite	$K_2O.3Al_2O_3.6SiO_2.2H_2O$
Albite	$Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$
Anorthite	$CaO.Al_2O_3.2SiO_2$
Kaolinite	$Al_2O_3.2SiO_2.2H_2O$
Gibbsite	$Al_2O_3.3H_2O$
Limonite	$Fe_2O_3.H_2O$
Serpentine	$3MgO.2SiO_2.2H_2O$

Correction was given for evaporation of methanol during agitation with the clay by carrying a blank. A photograph of the conductometric assembly is shown in Fig. 1.

Results and discussion

The chemical analyses of the clays are given in Table I and their mineralogical compositions as calculated by norm method are given in Table II.

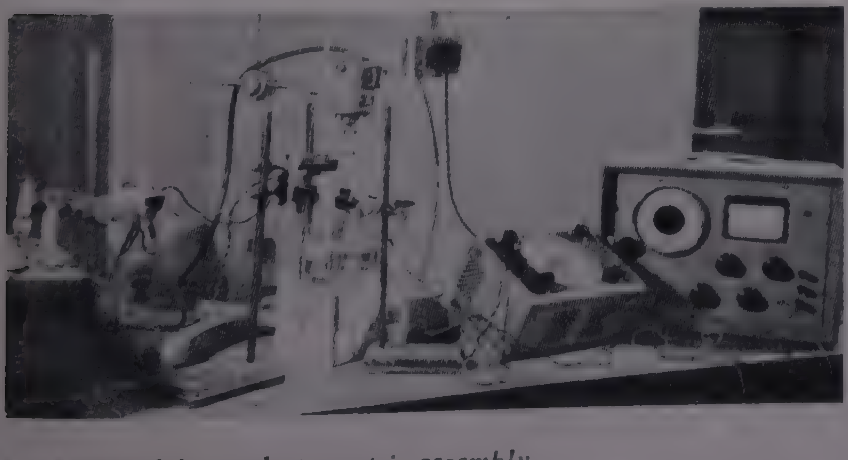
In calculating the mineralogical composition, information on non-clay impurities as revealed by X-ray analysis of the clay samples after heat-treatment at 700°C is taken into consideration.[5] Even though there are some assumptions without adequate evidence, this classical method of computing mineralogical composition gives an idea to a good approximation of the relative abundance of clay mineral and non-clay impurities. It is evident from the mineralogical composition, that the clays taken for this study not only contain the predominant clay mineral, kaolinite, but also some amount of non-clay impurities.

Base exchange and crystallinity of kaolinite

The 'bec' of the three clays viz., Travancore, Rajmahal and ball clays are as follows:

Travancore	6·9 me/100 gm
Rajmahal	11·1 me/100 gm
Ball clay	12·3 me/100 gm

The crystallinity of the clay mineral in the various clays was evaluated by the differences in their X-ray diffractograms, differential thermal curves and electron micrographs.



1 *A view of the conductrometric assembly.*

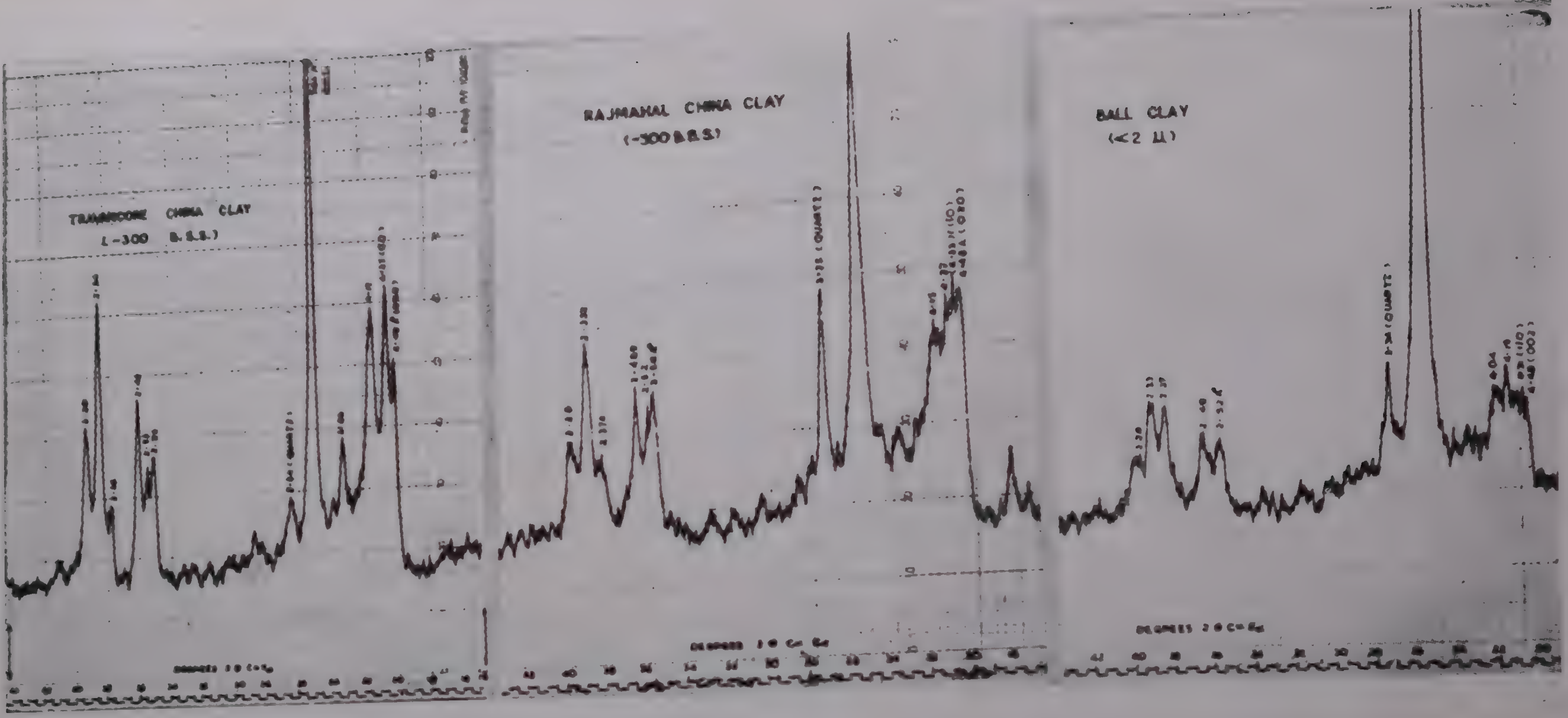
Brindley[6] had mentioned the characteristic difference, between a good kaolinite and a fire clay type mineral and the changes that are observed in the transition from a good kaolinite to a typical fire clay mineral. The typical fire clay gives a photograph which is generally weaker than that of kaolinite although for equal exposure conditions, the basal reflections are of comparable intensity to that of kaolinite. The high order reflections are fewer, broader and weaker than those from kaolinite. The two triplet groups of kaolinite (2·55, 2·52, 2·49 and 2·37, 2·33 and 2·28 K_x) disappear and are replaced by two pairs of medium strength lines. The (020)—(002) group of reflections are replaced by rather a weak band with a sharp head at 4·46 K_x. Judging from these conclusions, it is seen from Fig. 2 that the two triplet groups 34°—40° 2θ are most intense in the case of Travancore china clay and least in the case of ball clay. The first triplet group is replaced by a doublet in ball clay and the reflections are less intense and broader. Rajmahal china clay stands intermediate between Travancore china clay and ball clay. The X-ray evidence regarding crystallinity is in conformity with differential thermal curves and electron micrographs of the clays as shown in Figs. 3 and 4 respectively. Even though Rajmahal china clay stands next to Travancore china clay in crystallinity its 'bec' is much higher and it appears to be due to higher surface area and presence of halloysite impurity.

Even though the ball clay examined in the present study is structurally disordered as seen from X-ray and D.t.a., it is morphologically perfect. Its electron micrograph in Fig. 4 E shows a number of small crystals which exhibit completed hexagonal morphology. The same conclusions were arrived earlier by Robertson and Co-wrokers[7] regarding disordered kaolinite.

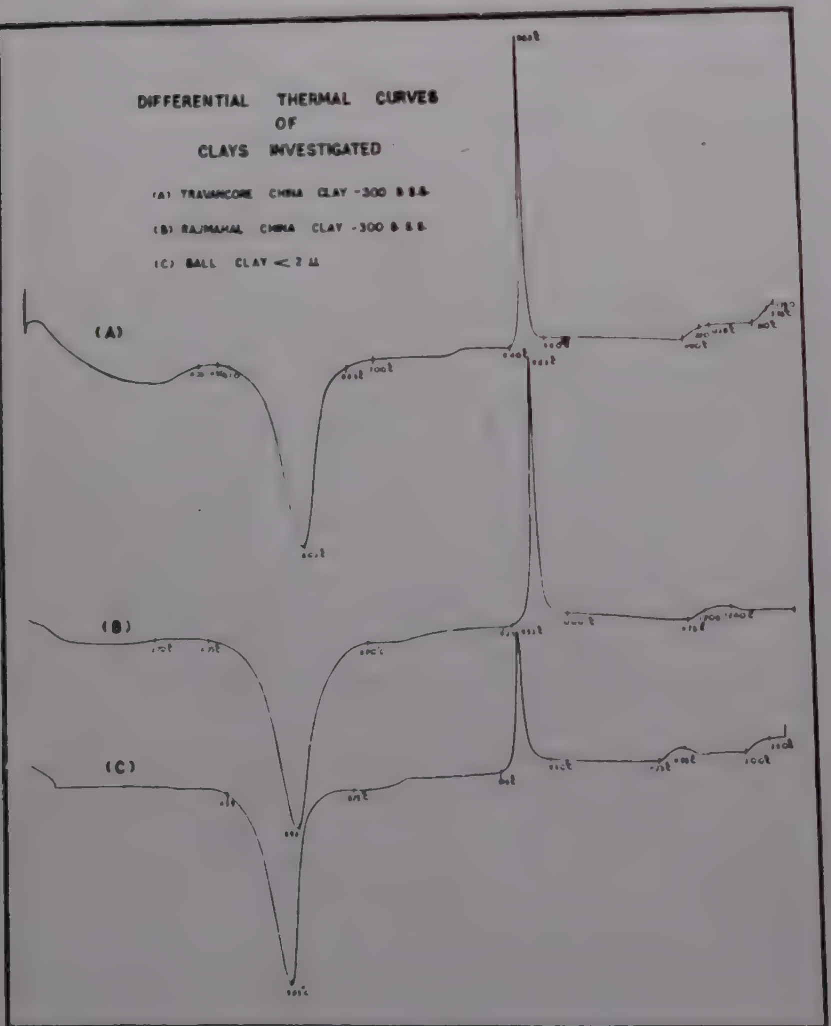
The observations in the present study that 'bec' increases with decrease in crystallinity in the order ball clay<Rajmahal<Travancore show that lattice distortions also will tend to increase broken bonds resulting in increasing 'bec' with decrease of crystallinity as observed by earlier workers.

Base exchange and surface area of kaolinite

Since the 'bec' of kaolinite is considered to be mainly a surface phenomenon due to broken bonds, increase of surface area should result in increase of 'bec' and this was shown to be true by a number of workers mentioned earlier in this text. With a view to see whether



2 *X-ray diffractograms of clays scanned through 16°-43 2θ for indicating differences in crystallinity. Radiation $C\mu K\alpha$, tube conditions = 30 kV, 20 m A, T.C. = 4, S.C. = 4, Scanning speed 2° min., chart speed 800 m.m./hr.*

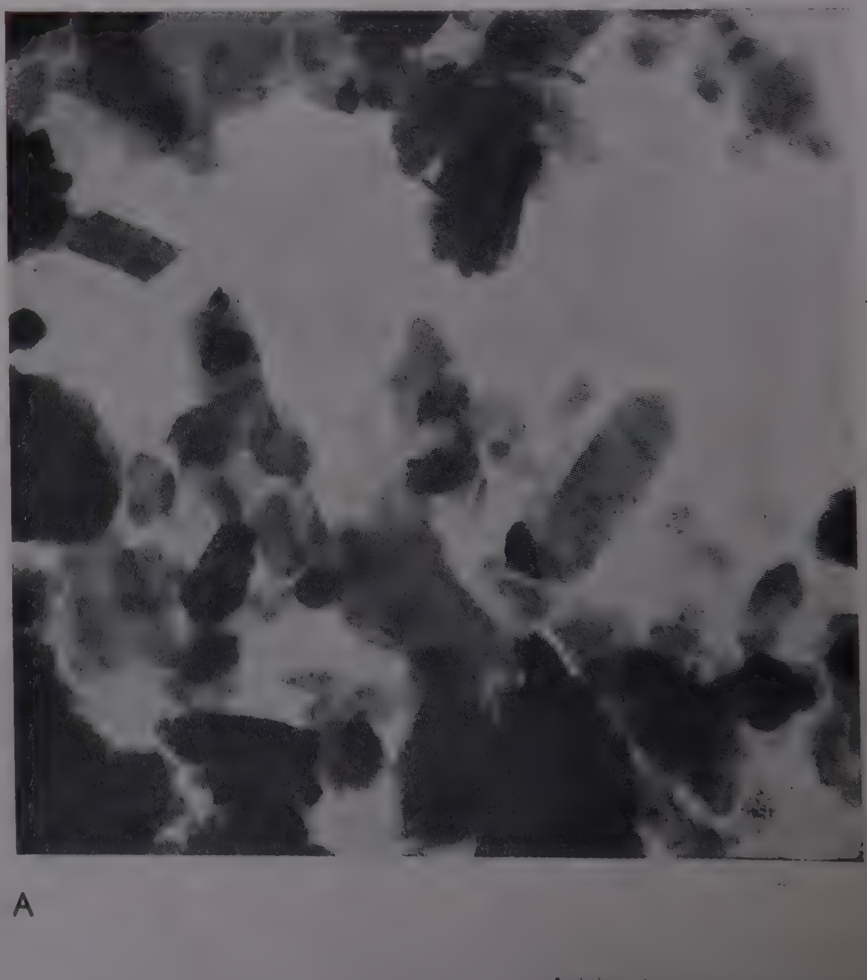


3

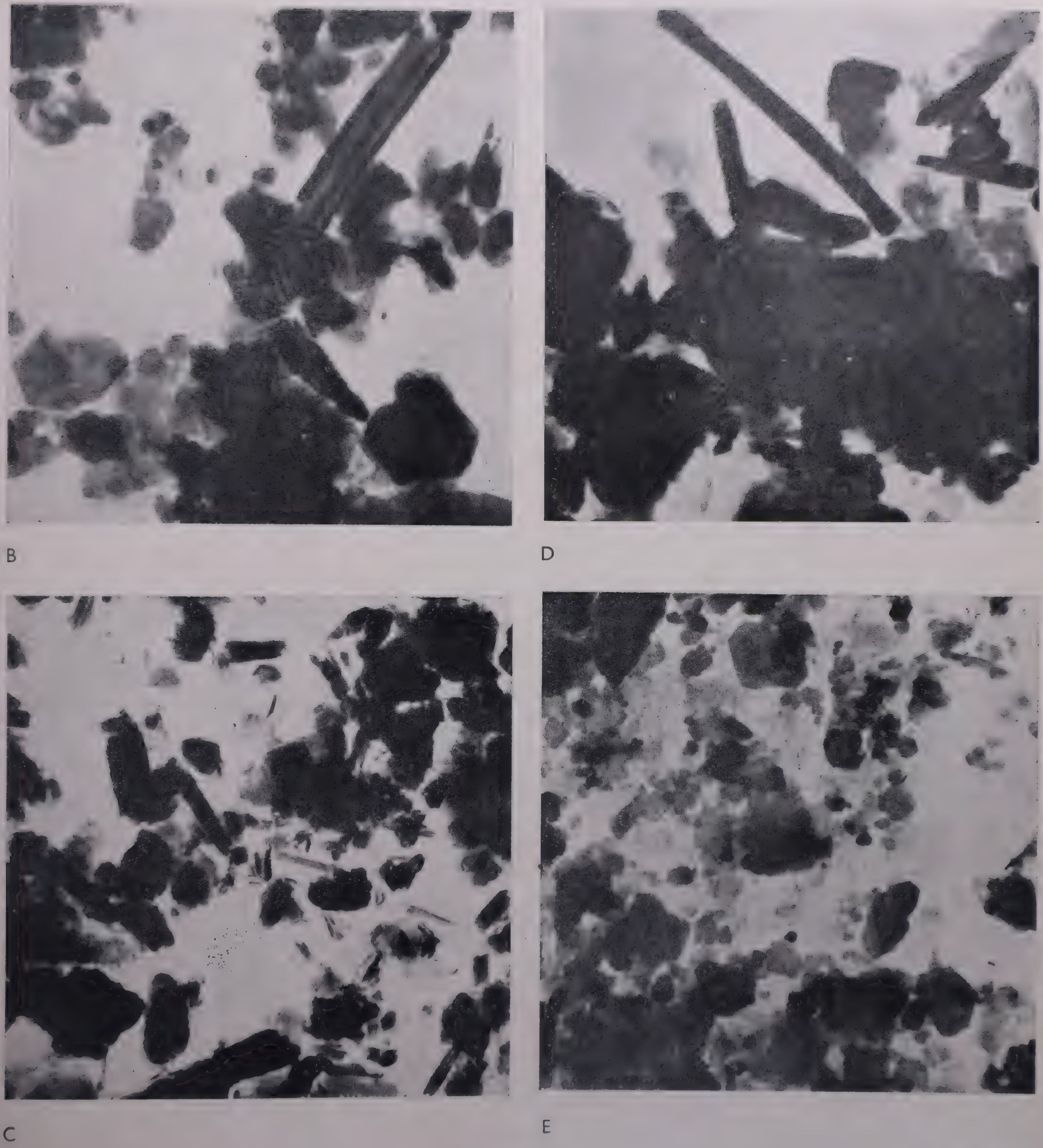
the same relationship holds good with different clays which are predominantly kaolinitic, the 'bec' of clays investigated were compared with their surface areas as determined by gas adsorption and liquid phase adsorption of stearic acid. Surface areas were determined by stearic acid adsorption also in order to compare the results with the more ideal gas adsorption technique which is rather complex. The results of 'bec' and surface areas by the two different techniques are given in Table III.

Even though Clyde Orr and Bankston[8] claimed good agreement between surface areas determined by stearic acid and gas adsorption methods, the results in the authors' study do not agree.

The results in Table III show that Travancore china clay has the lowest 'bec' and it agrees well in



A



A, B—Travancore china clay C, D—Rajmahal china clay E—Ball clay

4 *Electron micrographs of clays investigated. Magnification 1 cm = 1/2 μ*

relation to its specific surface as determined by argon adsorption but the values for Rajmahal and ball clays are not in agreement with their surface areas. This anomaly may be attributed to two reasons : (i) the ball clay is of the disordered or poorly crystallised type which may have greater number of broken bonds due to lattice distortions[7, 9] and possibly also there may be some limited isomorphous substitution leading to higher base exchange even though its specific surface is lower, (ii) the Rajmahal clay contains besides fine

TABLE III Base exchange and surface areas of clays

Sl. no.	Sample	Surface area m^2/gm. by stearic acid adsorption	Surface area m^2/gm. by argon adsorption at 90°K	Base exchange capacity me/100 gm at pH 8·8 by neutratisation of H-clay
1.	Travancore china clay —300 B.S.S.	10·7	8·6	6·9
2.	Rajmahal china clay —300 B.S.S.	28·0	19·0	11·1
3.	Ball clay $<2\mu$	8·8	16·0	12·3

grained kaolinite, some amount of tubular halloysite (Fig. 4 D) which can permit argon entry and adsorption on the internal surface of the tubes which may have a diameter of more than 250 A.[10] These considerations in the authors' opinion are responsible for the lack of direct relationship between surface area and 'bec' in the case of Rajmahal and ball clays. Increase of 'bec' with increase of surface area may occur within the same clay due to increase in broken bonds but it may not hold good when the base exchange capacities of different clays are compared with their surface areas due to some changes in the mineralogical composition of the different clays even though they are predominantly kaolinitic and also due to the presence of minerals like tubular halloysite which may contribute to internal surface area also.

Conclusions

X-ray evidence coupled with D.t.a. and electron microscopic studies has revealed that Travancore china clay is a relatively well crystallined kaolinite. Rajmahal ranks next to Travancore in crystallinity. Ball clay is a disordered kaolinite as evident from X-ray, D.t.a. and base exchange data. The base exchange of the clays increases with decrease of crystallinity of kaolinite in the different clays and this is in accordance with the findings of earlier workers. The surface areas measured by stearic acid adsorption according to the method adopted by Clyde Orr and Co-workers are not in agreement with argon adsorption data and the author feels that the results may not be comparable. Even though the 'bec' of a clay increases with its surface area, within itself base exchange capacities of different clays may not have a direct relationship with their surface areas due to some differences in their mineralogical composition and other factors which contribute to surface area. Even though the kaolinite in the ball clay examined is structurally disordered as seen from X-ray analysis, it is morphologically perfect as seen from its electron micrograph. These observations are in agreement with those of earlier workers.

Acknowledgements

The author expresses his deep gratitude to Dr B. R. Nijhawan, Director, National Metallurgical Labqratory for his invaluable suggestions during the work. Thanks are due to Sri H. V. Bhaskaral Rao, Scientist, Refractories Division for his critical appreciation of the paper and Sri B. N. Haldar, Scientist, for his co-operation in taking electron micrographs.

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Development of Superduty Silica Bricks with Indigenous Raw Materials

Gurubux Singh Minhas
H. V. Bhaskar Rao

Development of superduty silica bricks with indigenous raw materials which are known to be abundant, was investigated. Three samples of quartzites from Jamda, Mihijam and Hyderabad were studied. This study has revealed that crypto-crystalline variety of Jamda quartzite which is very low in alumina, can be used successfully for the manufacture of superduty silica brick by proper granulometric control, high pressure forming and firing under strictly controlled conditions. The product thus obtained has the requisite properties of a superduty quality brick. The addition of low aluminn quartztite fines to graded Mihijam quartzitedoes not effect any tangible improvement in the physical properties of silica brick specimen made out of the mix. However, appreciable improvement in porosity, permeability, refractoriness underload, etc. could be attained by proper forming and by improved processing methods as adopted in the case of Jamda quartzite. Low alumina quartzite from Hyderabad was not found suitable for making superduty bricks and even addition of fines from this quartzite to Mihijam quartzite did not bring out any improvement in the silica brick made from Mihijam quartzite, probably due to very friable nature of this low alumina quartzite from Hyderabad.

ACCORDING to American definition, bricks having 30—50°C higher refractoriness underload than common silica bricks and containing not more than 0·4 per cent alumina, titania and alkalies in additions to the usual 2 per cent lime bond are generally classified as superduty silica bricks. The two other characteristics of such bricks, which are equally important, are low porosity and permeability.

Superduty silica bricks give better service performance as compared to common silica bricks when used in open hearth furnaces. They give longer life, fewer shutdowns for repairs and consequently better output and less cost of production for steel.

The present day trend is towards all-basic open hearth furnaces and even the existing silica roofs are being gradually changed over to all-basic roof usage; however conversion of existing silica roof furnaces to all-basic open hearth furnaces involves radical changes in design, such as suspended roof and much higher cost, etc. As it is physically impossible to change over all existing furnaces from silica to basic because of many reasons, it should still be possible to get better life from open hearth furnaces having silica roof by using superduty quality in place of the common silica bricks. The well known advantages of superduty silica bricks as compared to common silica bricks as well as its merits and demerits as compared to basic bricks for open hearth roofs, have been reviewed by one of the authors.[1]

The demand for silica refractories in India by the end of the Fourth Five Year Plan (1970–71) has been estimated at 75 000 tons per annum.[2] Even if only 20% of the requirements are met by superduty quality, the tonnage involved would be considerable. At present superduty silica brick in the real sense of the term, is not manufactured in the country, in any organised manner or in appreciable quantity. Hence, the development of superduty silica brick with indigenous raw materials, which are known to be abundant, was comprehensively investigated in the National Metallurgical Laboratory.

Raw material

Impurities generally present in silica bricks have been classified into two main groups[3]: (i) those oxides such as Al_2O_3, TiO_2, alkalies, etc. which adversely affect the refractoriness of the brick and (ii) those such as CaO, MgO, BaO, etc. which when mixed in small percentages with silica and melted, produce immiscible liquids. Refractoriness of silica brick is said to be substantially improved by restricting the total amount of group (i) oxides to less than 0·4% and that of group (ii) oxides between 2·5 to 5%. Though alumina content of siliceous raw materials should be as low as possible which can be often achieved by proper selection and washing treatment of the raw materials, all silica minerals with low alumina contents will not produce good quality bricks. The porosity of the raw material must be low and its inversion characteristics must be slow and steady in order to avoid firing troubles such as shattering. Though the American definition classifies TiO_2 also as a deleterious ingredient along with Al_2O_3 and alkalies, the presence of a high percentage of TiO_2 in South African Silcrete[4] has not adversely affected its quality. On the other hand, it appears to have facilitated inversion at low temperature and produced a brick free from firing faults. In Germany,[5] superior quality silica bricks meant for open hearth roofs, are made from Findlings quartzites which contain 97–98% SiO_2 and 1 to 2% Al_2O_3, Fe_2O_3 and TiO_2. To this a high percentage of low alumina sand is said to be added.

It appeared from an earlier study by the present authors,[6] that the crypto-crystalline quartzite from Jamda area which is low in alumina content, could be employed for superduty silica bricks. Mihijam quartzite, which is being currently used for silica brick manufacture, could also be investigated for superduty quality by incorporating low alumina quartzite fines, proper dense packing and high pressure forming. Preliminary trials carried out in the earlier study with low alumina

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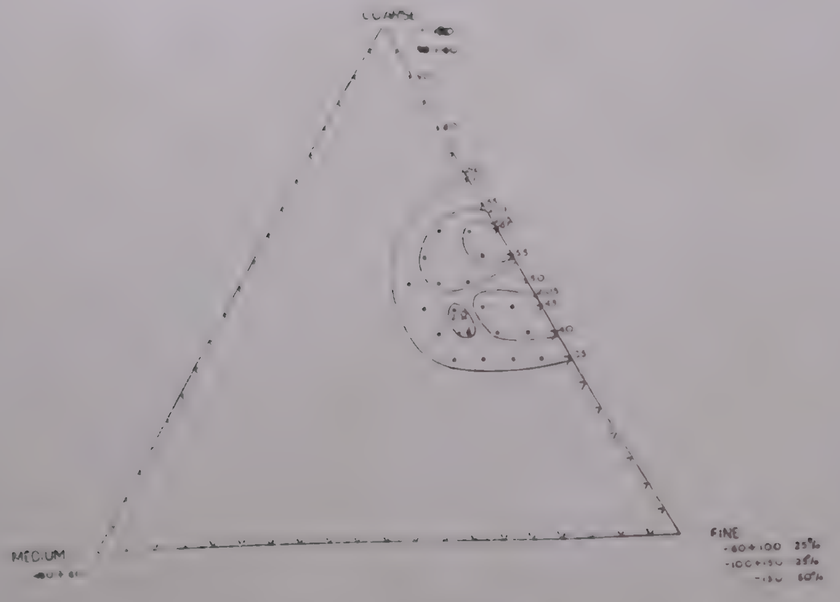
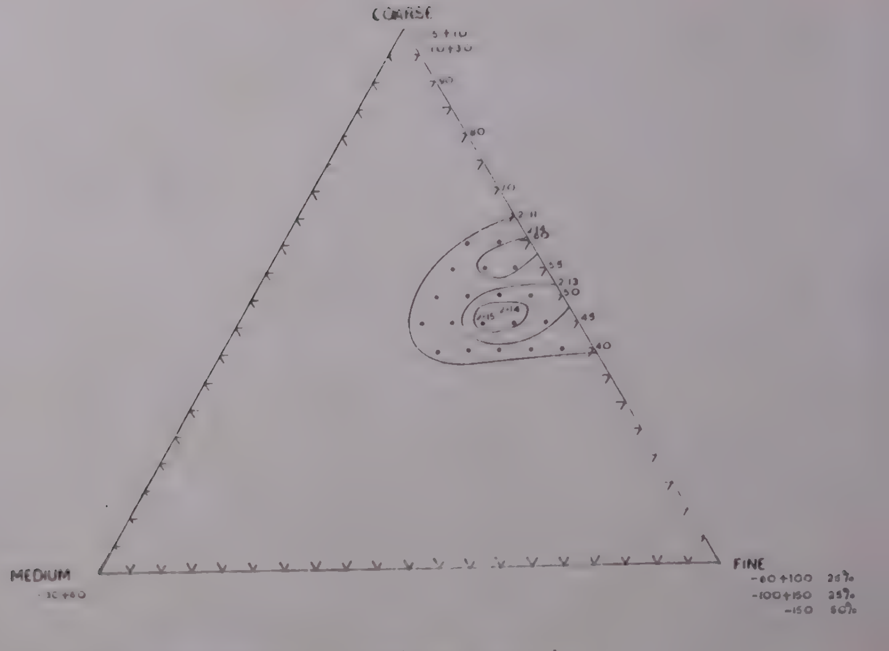


1 *Packing characteristics of Jamda quartzite.*



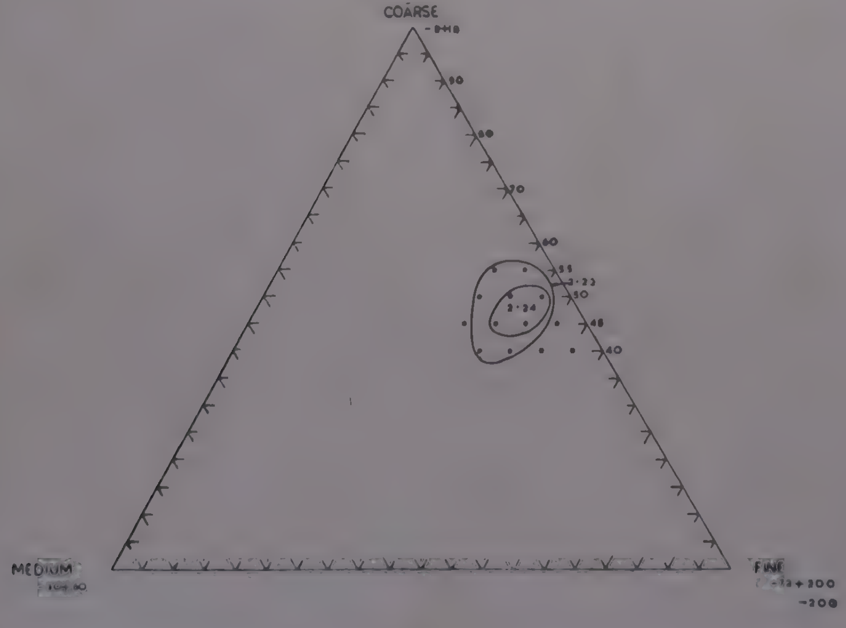
3 *Packing characteristics of Mihijam quartzite.*

quartzites from Hyderabad showed them to be too friable to be used by themselves. Hence in this study, Hyderabad quartzite fines only were incorporated as additions to Jamda and Mihijam quartzites but were exclusively used for making bricks because of their friable nature.

Experimental procedure

The three samples of quartzites from Jamda, Mihijam and Hyderabad, received in lumps of 2 to 4 inches were washed, as a routine, though this did not lower the alumina content as the raw materials were quite pure and clean to start with and there was no adherent clay material which could be washed out. The crushing characteristics of the raw materials were studied by passing known weights of material once through jaw crusher and roll crusher, keeping their gaps constant and sieving and weighing the fractions obtained. The 2 to 4 inches lumps were crushed in jaw crusher to $\frac{1}{2}''$ size and passed through a roll crusher to obtain -10 mesh. The material was sieved to different sieve fractions and fines were obtained by further grinding in ball mills. Packing density studies were carried out by blending the different fractions. Based on these studies, required gradings were prepared by further crushing of those grindings which were in excess of requirement. Suitable grain sizes thus obtained were blended together with 1% mill scale in the dry state. Two per cent calcium oxide was added in the form of milk of lime, and 4% sulphite lye was also added for green bond. The total moisture content of the mix was about 4%. In the last batch, a part of the coarse fraction was replaced by fired silica brick grog from the same material. The ingredients were mixed dry for 10 minutes before addition of milk of lime and sulphite lye and mixed again for another 20 minutes in a Simpson type mix muller. For the first batch, the forming pressure used was 10 000 lb/sq inch on 2″ dia. buttons and these were pressed in a 30-ton hydraulic press. For the second batch, full-size bricks were pressed at 200-ton total pressure in a 500-ton hydraulic press. Full-size bricks were also tamped using a pneumatic forge hammer with a 2 cwt tup which had been suitably adapted for tamping bricks. Hand moulding was also tried.

The buttons and full-size bricks were air dried first for a couple of days before drying at 110°C. The specimens were fired in a coke oven gas fired down-draft kiln having about $2\frac{1}{2}' \times 2' \times 2'$ setting space. The burners were on natural draft in the initial stages and were put on forged draft for attaining high temperature. Slow temperature schedules were followed which varied from batch to batch. The furnace was sealed at the



2 *Packing characteristics of Jamda quarizite.*

TABLE I Cheimcal analyses and P. C. E. values of raw materials

	Jamda	Hyderabad Raj K (3)	Hyderabad B (4)	Mihijam
Loss on ignition %	0·12	trace	trace	trace
Moisture %	0·07	0·04	0·04	0·04
SiO_2%	99·72	99·28	99·28	98·76
Al_2O_3%	0·04	0·20	0·21	0·84
Fe_2O_3%	0·06	0·04	0·03	0·10
TiO_2%	nil	trace	trace	0·02
CaO%	trace	0·24	0·32	0·22
MgO%	N.D.	trace	trace	trace
Alkalies %	nil	trace	trace	Na_2O 0·11 K_2O trace
P.C.E.	31–32	22		30-31

end of soaking period and cooled down to room temperature before the specimens were unloaded. Physical properties of the fired specimens were determined as per standard methods.

Results

The chemical compositions of the three raw materials and their P.C.E. are given in Table I. The crushing characteristics of the quartzites are given in Table II. The actual gradings used in the packing density studies and granulometric compositions which have given maximum pack-density are given in Table III. The results of packing density studies are plotted on triaxial graph and are shown in Figs. 1 to 3. The firing schedules followed for each batch are given in Table IV and the physical properties of the fired specimens are given in Tables V and VI. Figures 4 to 7 are the photomicrographs of polished specimens made from the final fired samples using Jamda and Mihijam quartzites.

Discussion

It may be seen from Table I that the alumina content of Jamda, Hyderabad(K) and Mihijam quartzites are 0·04, 0·20 and 0·84% respectively. Though addition of fines from Hyderabad quartzite is not likely to improve the properties of silica brick made from Jamda quartzite, in the case of Mihijam, it could effectively reduce the alumina content to bring it in line with the minimum specified for superduty silica brick quality, i.e. 0·4%. But, from the physical properties given in Table V, it may be observed that the addition of ball mill fines from Hyderabad quartzite has not substantially improved the properties of silica brick made from Mihijam quartzite. As a matter of fact, the porosity has slightly increased though the refractoriness underload appears to have improved slightly. Hence in the last batch, fines from Hyderabad quartzites were not incorporated.

From Table II, it may be observed that Mihijam and Jamda quartzites are quite hard and produce much less fines than Hyderabad quartzite which was very soft and friable, when all are treated under identical conditions. From Hyderabad quartzite, it is rather difficult to get enough coarse fraction, if it is to be used all by itself for silica brick making. The other two give the maximum quantity of −10+18 coarse fraction with very little medium fraction of −30+60 which is generally required in lesser quantity for good packing density. The excess of −10+18 fraction could be converted to ball mill fines, as required.

Packing density study

It is generally known that granulometric compositions of graded quartzite give the maximum packing density when the proportion of coarse, medium and fines are in the neighbourhood of 45 : 10 : 45. In order to select the best gradings as well as the proportions which would give the maximum packing density, two sets of continuous gradings and two of gap gradings (Table III) were tried.

TABLE II Crushing characteristics of raw materials

Grading	Mihijam	Jamda	Hyderabad Raj (K)
− 5+10	9·0	11·0	3·8
−10+18	68·2	68·9	28·1
−18+30	8·9	9·3	26·2
−30+60	6·0	3·7	19·0
−60+72	1·0	2·5	12·6
− 72	7·0	5·5	10·2

The maximum packing density obtained with Jamda quartzite is 2·24 and with Mihijam quartzite 2·19. It may also be observed from Table III that there is no appreciable difference in maximum packing density between the gap grading and continuous grading. Either one of them could be used depending upon the crushing characteristics of the quartzites.

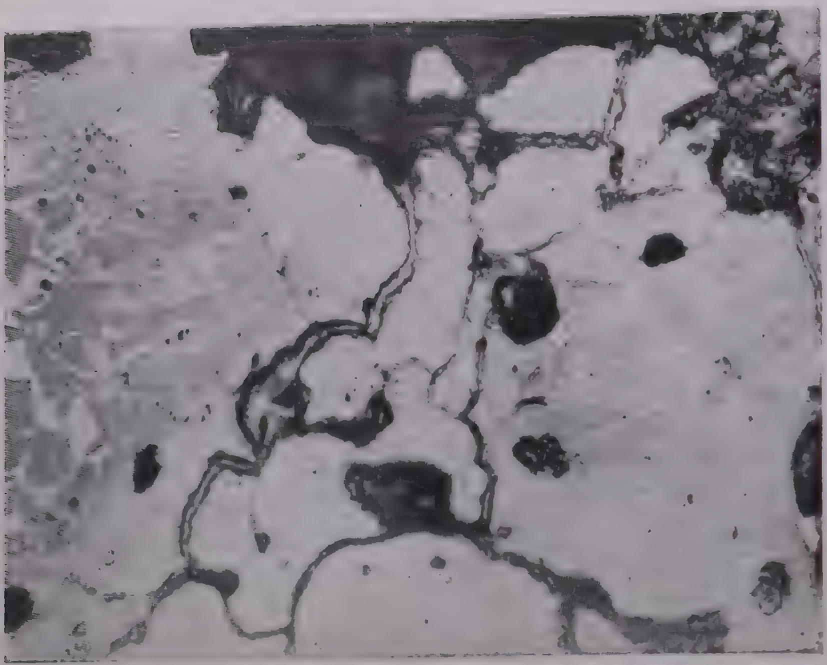
Out of the two firing schedules given in Table IV, it may be observed that in the one used for batch 2, the rate of rise has been lower and also the soaking has been given at 575°C. The rate of rise has also been slowed down further at 860°C to 900°C with a view to take care of the polymorphic change from quartz to tridymite expected to take place at this temperature. The rate of rise was slowed down between 1 200 and 1 300°C as it was expected that the inversion of high temperature form of quartz directly to cristobalite might take place at this temperature as it is well known that the transformation from quartzite to tridymite does not generally take place in the first firing. The maximum firing temperature was also lowered to 1 400°C for the 2nd batch in order to keep the temperature well within the stability range of tridymite.

Comparing Tables V and VI, changing the firing schedule to a slower rate of rise of temperature as has been done in the 2nd batch, seems to have produced the desired results, such as lower porosity and permeability, higher crushing strength and better conversion as indicated by lower specific gravity and reheat expansion. Slight improvement in refractoriness underload also may be noticed.

In the last batch, some full-size bricks were tamped by a pneumatic hammer adapted for tamping bricks. These bricks were given 20 tamps. From the physical properties, it appears these tamped bricks compare well

TABLE III Gradings, Granulometric compositions and packing density

Sl. no.	Coarse	Medium	Fines		Percentage of granulometric composition			Max. Packing density	Quartzite source
					C	M	F		
			(−60+100)	25%	45	15	40	2·15	Mihijam
(i)	−5+30	−30+60	(−100+150)	25%					
			(−150)	50%	40	15	45	2·20	Jamda
(ii)	−7+30	−30+60	(−60+100)	25%	45	10	45	2·18	Mihijam
			(100+150)	25%					
			(−150)	50%	45	10	45	2·10	Jamda
(iii)	−5+10	−30+52	(−72+100)	50%	55	5	40	2·18	Mihijam
			(−200)	50%	55	5	40	2·19	Jamda
(iv)	−5+18	−30+60	(−72+100)	50%	50	10	40	2·19	Mihijam
			(−200)	50%	45	10	45	2·24	Jamda

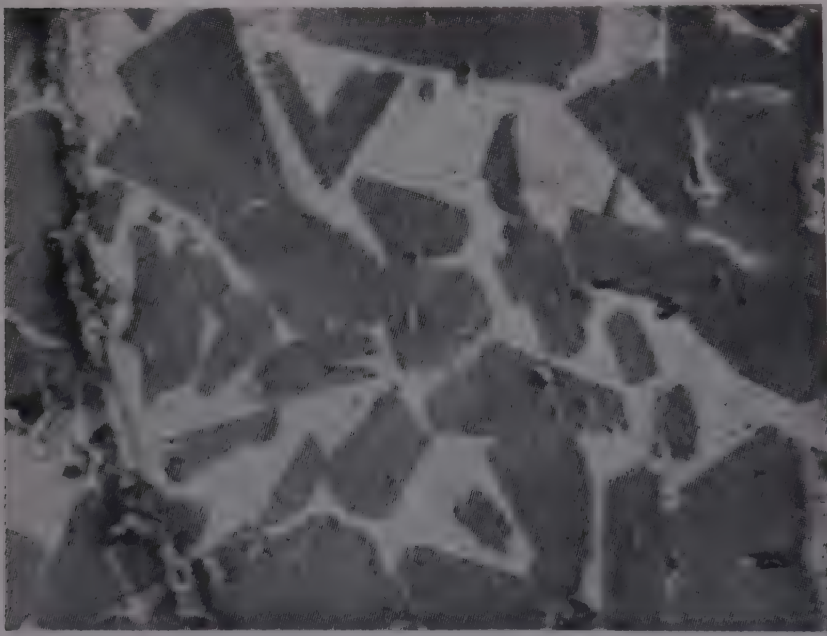


4 *Lath and wedge shaped crystals of tridymite (dark grey) in calcium silicate glass (bright) surrounding grains of cristobalite (lower portion)*
Reflected light magnification. 165

TABLE IV Firing schedule

Batch No. I	Batch No. II
Up to 400 C—15 C hr.	Up to 550 C—10 C hr
400 C to 550 —10 C hr.	550 C to 575 C—5 C hr
550 C to 600 —5 C hr.	575 C—5 hours soaking
600°C to 650°C—10°C/hr.	575°C to 860°C—15°C/hr
630°C to 1450°C—25°C/hr.	860 C to 900 C—5 C/hr
1450°C—24 hours soaking	900 C to 1200 C—20 C/hr
	1200 C to 1300 C—5 C hr
	1300 C to 1400 C—15 C hr
	1400 C—24 hours soaking

with those pressed at 10 000 lb/sq inch. As expected, the hand moulded shape had a higher porosity and permeability and lower crushing strength as well as refractoriness underload, which can be attributed to the lower bulk density. From this study, it appears that practically no improvement has been achieved by the incorporation of lower alumina quartzite fines. As a matter of fact, the porosity appears to have increased and the crushing strength lowered slightly, which may be due to the extremely friable nature of the low alumina fines used in this instance.

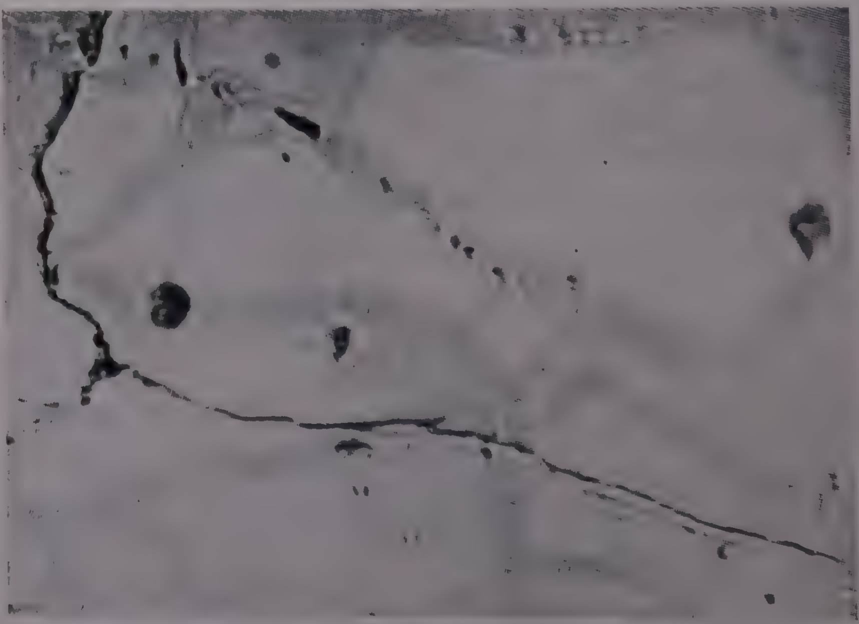


5 *Well developed tridymite wedges and tablets in calcium silicate glass.*
Reflected magnification 420

6 *Tridymite and cristoballite crystals (grey) calcium silicate matri (bright).*
Reflected light magnification 420.

Mineralogical composition of fired specimen

From the photomicrographs of polished sections shown in Figs. 4 to 7, it may be observed that conversion to tridymite is quite pronounced in the case of specimen from Jamda quartzite. On the other hand, in the specimen made from Mihijam quartzite, especially in batch I, there is some unaltered quartz. This is also indicated by the higher reheat expansion as shown in Table V.



7 *Quartz rich portion of the specimen showing conversion of quartze to crystobalite along net work pattern.*
Dark grey veinlets—Crystobalite.
Light grey area—unaltered quartz.
Reflected light magnificatian 420

TABLE V Physical properties of batch I

	Physical properties								
Quartzites used	Specific gravity gm/cc	Bulk density	Apparent porosity	Refractorincss underload		Compression tests kg/sq ft	Linear reheat expansion	Permeability C.G.S.	Quality index
				ta °C	te °C				
Mihijam	2·35	1·80	23·5	1680	1700	154·5	1·3	8×10^{-2}	33·6
Mihijam (Rajk fines)	2·330	1·77	25·5	1700	1710	149·6	1·2	9×10^{-2}	33·5
Jamda	2·336	1·85	23·5	1684	1715	164·3	1·0	5×10^{-2}	24·0

TABLE VI Physical properties of batch II

	Physical properties								
Quartzites used	Specific gravity gm/cc	Bulk density	Apparent porosity	Refractoriness underload		Compression test kg/sq ft	Linear reheat expansion	Permeability C.G.S.	Quality index
				ta °C	te °C				
Mihijam pressed	2·332	1·82	21·0	1 710	1730	175·0	0·7	3×10^{-2}	31·0
Jamda hand moulded	2·340	1·73	25·0	1 665	1685	103·2	1·0	22×10^{-2}	25·5
Jamda pressed	2·335	1·82	19·0	1 700	1 710	189·5	0·15	$3·5\times10^{-2}$	19·5
Jamda tamped	2·335	1·85	19·5	1 705	1 730	192·8	0·15	$4·0\times10^{-2}$	20·0

In Tables V and VI, the quality index for these bricks has been calculated as suggested by Konopicky[7] who has stated that the over-all figure of porosity plus 12 times the alumina content was usually less than 40 for normal roof bricks and less than 25 for bricks used in fast operating furnaces. From the quality index figures given in Tables V and VI, it may be observed that the superduty compositions developed with Jamda quartzite have a quality index below 25 due to its very low alumina content coupled with low porosity obtained by high pressure forming and controlled firing. The hand-moulded brick need not be considered from this point of view as it does not come under the classification of superduty brick, because of its high porosity. That the addition of low alumina fines to Mihijam quartzite has not improved its properties, to be classified as a superduty brick, is also evident from the fact that there is no difference in the quality index with and without additions of low alumina fines.

Conclusion

This study has revealed that crypto-crystalline variety of Jamda quartzite which is very low in alumina, can be used successfully for the manufacture of superduty silica brick by proper granulometric control, high pressure forming and firing under strictly controlled conditions. The product thus obtained has the requisite properties of a superduty quality brick.

The addition of low alumina quartzite fines to graded Mihijam quartzite does not effect any tangible improvement in the physical properties of silica brick specimen made out of the mix. However, appreciable improvement in porosity, permeability, refractoriness underload, etc. could be attained by proper forming and by improved processing methods as adopted in the case of Jamda quartzite.

From the economic point of view also, manufacture of superduty quality silica brick from Jamda or Mihijam quartzite should be feasible, as the only major difference in the manufacturing process is the high pressure forming together with proper control over grain size and firing schedules. The higher cost involved in installing heavy duty presses capable of welding pressure of the order of 100 lb/sq inch and above will be offset by the better quality of the brick and the better price it will fetch.

Acknowledgements

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Some Observations on the Effect of Heat Treatment on Stress Corrosion Cracking of Hardenable Steel

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B. R. Nijhawan

Martensitic stainless steels when heat treated to very high strength level have been known to be susceptible to stress corrosion cracking under substantially milder corrosive conditions, such as marine or semi-industrial atmosphere. The heat treatment, type of corrosive envirorments, etc. have been found to have a great influence on the cracking time. In the present paper the authors discuss the effect of tempering temperature and hardness level on the stress corrosion behaviour of 12% chromium stainless steel on the basis of tests carried out by them and the results reported in literature.

Tests were conducted in acidic chloride solution containing H_2S, which promotes entry of hydrogen into the steel. In such media tempering temperature was found to be very important as regards the susceptibility to cracking. Steels tempered above 600°C was found to be immune to cracking. Maximum susceptibility was found for steels tempered at temperatures between 400 and 500°C. The results have been discussed on the basis of changes in physical properties, the type of precipitated carbides and hydrogen embrittlement.

AMONGST various high strength alloy steels the hardenable straight chromium stainless steels occupy a unique position as they can be imparted high strength by proper heat treatments. In addition, these alloys have high resistance to general corrosion under many conditions. They are, however, susceptible to spontaneous cracking in corrosive environments in presence of tensile stress. Ffield[1] and Gerard[2] reported cracking of 13% Cr–0·2% C steels when exposed to sea water or salt spray. Uhlig[3] first showed that 12% Cr steels crack very rapidly under stress in salt water when coupled to aluminium or charged with hydrogen cathodically. At the Symposium on 'Sulphide Stress Corrosion' in 1952[4] the problem of cracking of high strength alloys was discussed at length. Bloom,[5] Lillys and Nehrenberg[6] and in the recent years Phelps[7,8] have carried out detailed studies on the effect of various factors on stress corrosion cracking of high strength steels under different conditions. The mechanism of cracking of high strength steel has, however, been subjected to considerable speculation. Some investigators have suggested that cracks are caused solely by hydrogen embrittlement while others have attributed their formation to the presence of preferred localised paths for corrosion. On the other hand Fraser and Treseder[9] and Bloom[5] have proposed a combined mechanism.

An investigation was undertaken at the National Metallurgical Laboratory to explore the effect of heat treatment, composition, stress level and corrosive media on the stress corrosion cracking of hardenable stainless steel. The aim of the investigation was to study the mechanism of stress corrosion cracking and correlate the various metallurgical and electro-chemical factors with cracking susceptibility.

The paper presents some of the interesting results observed in the initial phase of the investigation. The results have been discussed on the basis of known changes taking place during tempering and the probable effect of the same on the cracking susceptibility. The paper further discusses the line in which the subsequent work will be carried out to throw more light on the mechanism of cracking.

Experimental procedure

Materials

All tests were carried out with 12% Cr hardenable steel. For comparison 17% Cr ferritic stainless steel and 18 Cr–8 Ni austenitic stainless steels were also included in the studies. Composition of the alloys tested is given in Table I.

TABLE I Chemical composition of the materials used

Alloy No.	Cr	Ni	Mn	Si	C	Fe
	Chemical composition (%)					
1.	11·69	—	0·42	0·18	0·19	rest
2.	16·94	—	0·32	0·16	0·05	rest
3.	17·97	8·98	0·30	0·18	0·08	rest

The alloys were prepared in 20 lb high frequency furnace, using mild steel scrap and high grade ferro-alloys. The alloys after melting were deoxidised and then cast in two ingots of 2½″ square cross section. Hot top was used during casting to ensure production of sound ingots. The ingots were hot forged at 1 050–1 100°C and then hot rolled to 0·05″ thick sheet form. The alloys were descaled and annealed at 1 000°C. The annealed sheets were then cold rolled to the final

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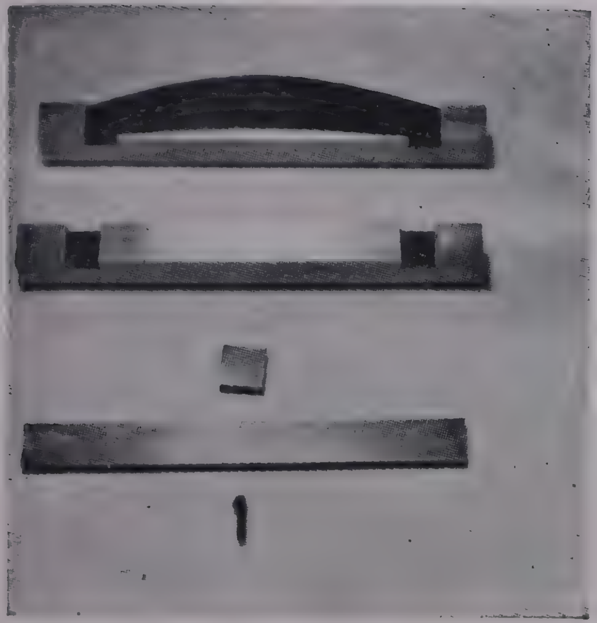


1 *Method for stressing specimen.*

2 *Experimental set-up for stress corrosion cracking studies.*

thickness of 0·03″. From the cold rolled sheets, samples of required sizes were made.

Preparation of sample

Tests were made with bent beam specimen of type shown in Fig. 1. The holder was made of 18/8 Cr—Ni stainless steel. The holder span used was 4″. The thickness of the specimen was 0·03″ and the width ½″. All the specimens were loaded to the stress level of about 80 000 lb/sq in, for which the appropriate length of the specimen was determined from the relationship given by Phelps et al.[7] The specimens were sheared from the sheet to the proper width and to a length of 4·5″, which was longer than that which was to be used for the tests. All specimens were made longitudinal (parallel) to the rolling direction.

Heat treatment

The samples were heat treated in argon atmosphere, Samples were heated to a temperature of 1050°C. homogenised for 1 hour and then quenched in water. The quenched samples were then tempered at different temperatures for 2 hours and then air cooled. After heat treatment the specimens were polished to a finish by 'O' grade emery paper. Care was taken not to unduly heat up the surface of the specimens during surface preparation. The specimens were then cut to the appropriate length to produce the desired stress after bending. The excess portion of the sample was used for determining the hardness after the heat treatment. The specimens were degreased by rubbing with MgO paste, washed with distilled water and then rinsed in acetone. The specimens were then stored in a dessicator until the tests were to be carried out.

Test media

Various test media have been used for studying the stress corrosion cracking of heat treatable stainless steels, e.g., salt fog test, atmospheric corrosion test, etc. Of these the most severe media has been found to be those which promote hydrogen embrittlement and contain mixture of chloride, acid and sulphide.

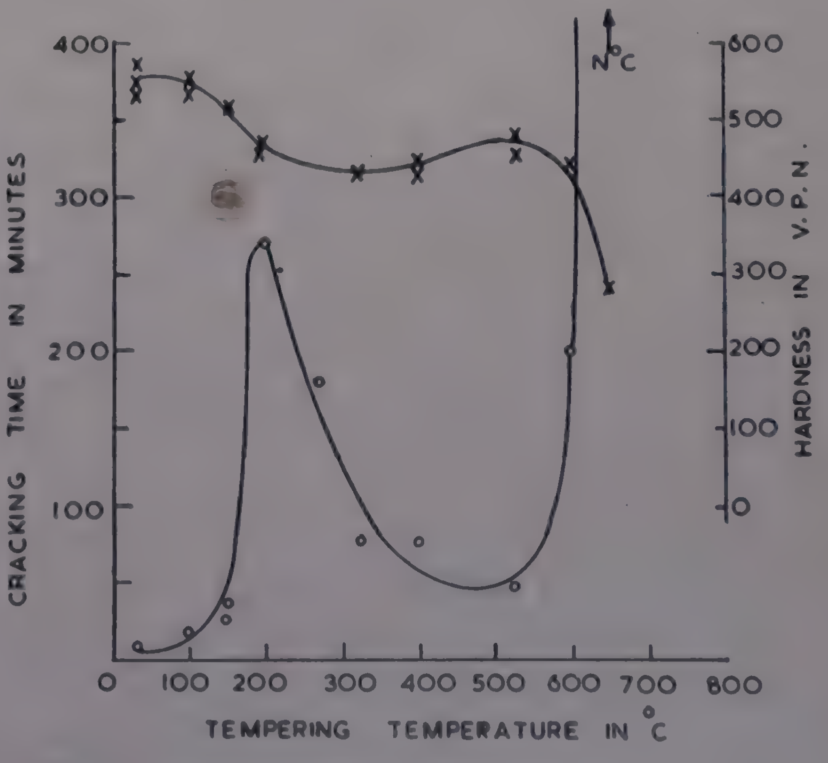
There are controversies as to the mechanism of cracking in different media. In this investigation, the tests were conducted in a 6% sodium chloride solution of distilled water containing 0·5% acetic acid. The solutions were saturated with hydrogen sulphide by bubbling H_2S gas for five minutes prior to the starting of the test. The study of the influence of other media will be taken up in near future.

Test procedure

Bent beam samples along with the sample holders, were coated with wax leaving bare an approximate area of 2 sq.cm. at the centre. The samples were immersed in the solution till cracking occurred. During the testing period, the potential of the corroding sample was periodically measured against saturated calomel electrode. The arrangement for testing is shown in Fig. 2.

Hardness and metallographic studies

Excess portions from the heat treated samples were polished to a finish by 'OO' emery paper and hardness



3 *Effect of tempering temperature on cracking time.*

was measured in Vickers Hardness Testing machine at 30 kg load. The metallographic study of heat treated and cracked samples was carried out by mounting the specimens, polishing and then etching them. The preparation of the specimen for microscopic study was carried out carefully to avoid the change in structure due to the heating of the sample during grinding and polishing.

Results and discussion

Effect of tempering temperature on hardness

Except 12% Cr steel, the other two steels tested did not form martensite on quenching. The 17% Cr steel showed completely ferritic structure after quenching with hardness value of 140 VPN. Similarly 18/8 Cr-Ni stainless steel, after heat treatment was completely nonmagnetic indicating the structure to be austenitic.

On tempering at various temperatures the variations in hardness of 17% Cr and 18/8 Cr/Ni steels were found to be little. On the other hand 13% Cr steel showed a systematic change in hardness as will be evident from Fig. 3 where the change in hardness has been plotted against tempering temperature. It will be evident from this curve that with increase in tempering temperature the hardness continuously decreased after about 150°C. Above 325°C slow increase in hardness was observed. The maximum secondary hardness effect, as can be observed from Fig. 3, occurred at temperatures between 450 and 500°C. Tempering at temperatures above 600°C showed a sharp decrease in hardness.

Effect of tempering temperature on cracking time

The effect of temperature on the stress corrosion behaviour of 12% Cr stainless steel is also plotted in Fig. 3. The results of the test clearly indicate that tempering temperatures of 600°C and above make the steel immune to stress corrosion cracking. The alloy was found to be highly susceptible to cracking in 'as quenched condition'. With increase in tempering temperature the cracking time increased, becoming maximum at 200°C. With further increase in the tempering temperature the cracking time decreased markedly, the susceptibility becoming maximum at tempering temperatures of 400–500°C.

Effect of time of tempering on cracking time

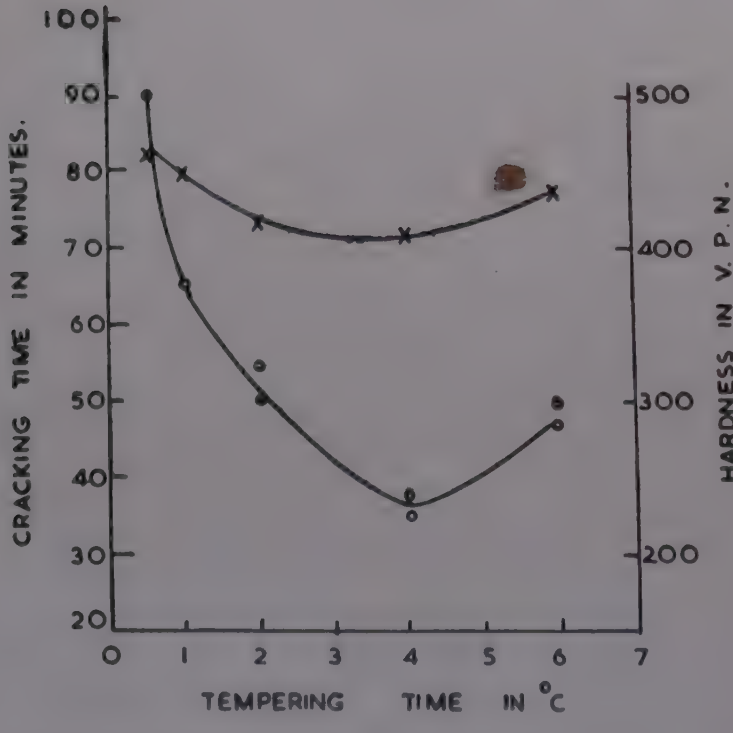
The effect of times of tempering in the sueceptible range, was studied on samples tempered for ½, 1, 2, 4 and 6 hours. The change in hardness and cracking time of samples tempered at 400°C have been plotted against tempering time in Fig. 4. It can be seen from Fig. 4 that with increase in tempering time the hardness decreases with corresponding increase in cracking susceptibility. The hardness value shows slight increase after 4 hours, though there is no corresponding marked change in cracking time.

Electrode potential of the samples during testing

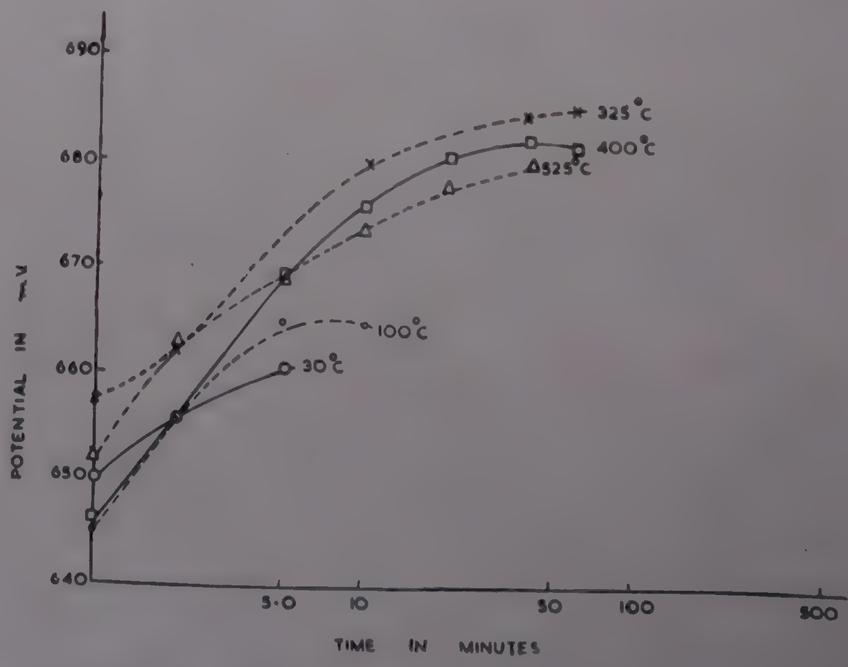
Electrode potential of the sample under test was measured during testing. The results of potential versus time have been plotted in Fig. 5. It will be evident from the figure that potential in the corroding system is negative and varies between 665 and 680 MV. With time the potential slowly changed to more negative value, at first more rapidly and then slowly. Tempering temperature was found to have some effect on corrosion potential. Sample in 'as water quenched' condition showed less negative value than those tempered at higher temperatures.

Appearance of stress corrosion crack and metallographic study

Failed specimens were examined metallographically to ascertain the nature of the cracking produced and structural changes occurring due to tempering. Grain boundary precipitation at prior austenitic grain boundary was found to start round about 450°C and became prominent at 520°C. Tempering temperature above 600°C was found to be very general and was clearly indicated



4 *Effect of tempering time at 400°C on cracking time.*



5 *Change in potential with time.*

by a sharp drop in hardness value. Attempts were made to isolate the carbides by anodically dissolving the steel in 5% HCl. Except for the sample tempered at 600°C, it was not possible to get good amount of residue for their identification. Examination of isolated residue indicated the carbide from the sample tempered at 600°C to be $Cr_{23}C_6$. The examination was made with CrKα radiation using a camera of 11·6 cm radius.

Failed specimens indicated the cracking to be both transgranular and intergranular, of the two the former predominating over the latter. Purely intergranular cracking was not observed in any case. Samples tempered up to 400°C showed purely transgranular cracking, while the same tempered above 400°C showed mixed cracking. These observations have been found to be similar to those of Lillys and Nehrenberg.[6]

17% Cr and 18/8 Cr/Ni stainless steel

Both the above steels were found to be immune to cracking and none of the samples failed even after a test period of 30 days.

Discussion

In discussing the mechanism of stress corrosion cracking of hardenable stainless steel it is necessary to consider the effect of various physical and chemical aspects associated with it. In the present studies the tests were carried out mainly in solution which facilitated absorption of hydrogen by steel. However to have a general outline of the mechanism of cracking the results of other authors on cracking in different media have also been discussed.

As the cracking is found to be greatly dependent on heat treatment, it is necessary to consider the effect of tempering on structural and mechanical changes. Steel, quenched from the austenitising temperature, consisted mainly of martensite. On tempering, the martensite decomposes and the structure undergoes series of changes depending on tempering temperature. With increase in tempering temperature there is first release of internal stresses and martensite loses its tetragonality. These changes are reflected in the initial decrease in hardness. At about 200°C the precipitation of carbides starts taking place. With increase in tempering temperature the nature and type of carbides precipitating also changes. Though chromium carbides are more stable in the initial stages Fe_3C is precipitated first. The duration of stability of Fe_3C is largely dependent on tempering temperature. At 200°C, the Fe_3C is found to be quite stable and persists even after tempering period of one to two hours. With further increase in tempering temperature the chromium carbides are formed; first Cr_7C_3 is formed which is followed by $Cr_{23}C_6$. These reactions can be represented by

$$Fe_3C \rightarrow Cr_7C_3 \rightarrow Cr_{23}C_6$$

These changes in the formation of different carbides are reflected in changes in hardness. As formation of Fe_3C and change from Fe_3C to Cr_7C_3 is thought to occur by in situ transformation[10,11] a continuous decrease in hardness is observed with increase in tempering temperature. The hardness versus tempering temperature curves, shown in Fig. 3, indicate that secondary hardening is observed when the martensitic stainless steels are tempered at temperatures above about 500°C. This secondary hardness can be attributed to the resolution of Cr_7C_3 prior to the formation of $Cr_{23}C_6$.

These structural changes have profound influence on room temperature Izod impact values in addition to that on hardness and other mechanical properties.[12] The initial martensite makes the steel very brittle with very low impact values. With increasing tempering temperature the value increases becoming maximum round about 230–250°C, corresponding to the stage at which cementite is precipitated, and the susceptibility to cracking decreases. Once the carbide starts precipitating, the impact value again decreases becoming minimum in the temperature range where the secondary hardening is observed and soon $Cr_{23}C_6$ starts forming the impact value and again increases with increase in tempering temperature.

Initiation of brittle fracture

Ferritic stainless steel may become susceptible to brittle failure, as cleavage failure can occur more readily in body centred cubic structures and not face centred cubic materials. Stroh[13] introduced the concept of a dislocation pile up in a slip band as supplying the condition for the initiation of cleavage crack; the pile up producing a stress concentration equivalent to that of Griffiths crack. Cottrell[14] has modified Stroh's initial observation by proposing that dislocations travelling on two intersecting (110) slip band can produce a dislocation pile up in the form of a giant dislocation with a Burgers vector nb which acts as a fine crack. The overall picture of initiation of brittle fracture is however still incomplete in spite of considerable work on the subject though it can be said that it is understood better for b.c.c. metals and alloys than f.c.c, ones. Of the various factors affecting the transition from ductile to brittle failures the more important ones are the rate of straining, alloy composition, heat treatment and hydrogen content.

The role of hydrogen in brittle failure

Effect of hydrogen content on the ductility of mild steel and alloy steels has been extensively studied by Troiano et al,[15, 16, 17] Baldwin et al[18, 19] Horzert[20, 21, 22], etc. These studies have considerably helped in the understanding of mechanism of hydrogen embrittlement. Hydrogen is known to go in interstatial solid solution. Hydrogen dissolved is distributed both in solid solution and in voids in the metal lattice. It is now agreed that hydrogen in voids actually embrittles the steel and embrittlement for any particular condition is dependent on the high density of hydrogen maintained in the voids by the hydrogen diffusing through the lattice. The time to failure after the diffusion of hydrogen in the steel is determined by the amount of hydrogen entering the steel. According to Troiano[17] with increase in the hydrogen charged, which is a function of charging current density, the time for delayed failure shows a sudden decrease at a particular current density. After this, increase in charging current has no effect on cracking time. A second sharp decrease occurs at a still higher current density when the specimen cracks during the period of charging itself. At this stage, known as irreversible embrittlement, the cracking time becomes independent of the cathodic currrent density. It is interesting to note that after this critical current density there is no increase in the amount of hydrogen picked up by the metal.[17]

Effect of tempering on corrosion

With increase in the tempering temperature, as discussed previously, the type and amount of carbide precipitated vary. In the initial stages, when only cementite is precipitated there is no marked change in corrosion rate. However, when chromium carbides are precipitated above 500°C along prior austenitic grain boundaries, the alloy becomes susceptible to corrosion. This is because of the fact that carbon ties up chromium equivalent to 12–16 times its own weight thus reducing the amount of chromium that is retained in solid solution. Since at low temperatures the carbides are precipitated at grain boundaries, and due to lower diffusion rate of chromium the matrix adjacent to the carbide is depleted in chromium, thus making it susceptible to corrosion.

Any theory to explain the mechanism of stress corrosion cracking in hardenable stainless steel should take into account all of the various factors noted above. The question of whether the cracking of martensitic stainless steels in chloride and other environments is due to hydrogen embrittlement or stress corrosion cracking is a most intriguing one and experimental results have been explained on the basis of one or the other theory. The tests carried out in the present experiments have been based in solution which definitely helps in the evolution of hydrogen and promotes hydrogen absorption. Cracking time vs tempering temperature in these tests, and tests carried out by other authors in similar solutions show the same trend. Comparison of this result with the impact value curve clearly indicates that both these curves follow the same general pattern. On the other hand tests under salt spray condition and atmospheric condition indicate that susceptibility is maximum in the tempered condition only, untempered steels showing higher resistance to cracking.

The susceptibility and transgranular nature of cracking in steels tempered up to 400°C, are probably connected with the hydrogen embrittlement. Role of hydrogen diffusing inside the steel becomes more clear if one considers the fact that in a few tests carried out without addition of H_2S, the cracking time increased by a factor of 100 and more.

The greater suscepitibility of untempered steel, it may be mentioned in this connection, is probably due to the combined effect of high internal stresses and lower impact values of the steel. The intergranular nature of cracking of steels tempered between 450 and 520°C is probably connected with the presence of highly anodic continuous corrosive path along the grain boundaries. In this case the initiation of stress corrosion cracking can be considered to be associated with the development of corrosion fissures. Once a fissure of critical length and radius, required to establish the necessary stress field around the base of the corrosion fissure, is created the fracture can be triggered and crack travels at high velocities. This type of failure can be visualised on the basis of purely a mechanical propagation. The crack may travel to the full length across the specimen or may be arrested due to release of stress at the crack tip or by encountering a softer area. This is probably the reason why presence of delta ferrite has been found to decrease the susceptibility to cracking markedly. Presence of hydrogen is however expected to further increase the susceptibility to brittle fracture.

But in salt spray test and atmospheric corrosion, the solution potential is expected to be much more positive than that required for the reaction $2H^+ + 2e \rightarrow 2H \rightarrow H_2$ to occur. According to Hoar[23] this reaction can occur in cases where pH is below 2. It is therefore difficult to see how hydrogen can be produced from less mildly corrosive conditions under which these alloys are known to be susceptible to corrosion cracking.

In this connection anodic and cathodic polarisation studies by Phelps et al[17] are of much interest. They showed that both anodic and cathodic polarisation increases the susceptibility of 12 MoV steels. On the other hand they did not find any effect of anodic and cathodic polarisation on cracking time of type 410 (15% Cr-0.12% C) alloys. These studies clearly indicate the role played by carbides, precipitated during tempering, in making the hardenable stainless steel susceptible to cracking.

Conclusion

Consideration of various factors clearly indicates that the mechanism of stress corrosion cracking of heat treatable alloy steels is not yet fully understood. In the authors' opinion it requires greater study on the lines noted below :

1. Effect of tempering temperature on the anodic and cathodic polarisation characteristics of heat treatable alloys.
2. Effect of tempering on amount of hydrogen absorbed and susceptibility to hydrogen embrittlement.
3. Effect of anodic and cathodic polarisation on cracking susceptibility.
4. Proper correlation of physical properties, corrosivity and hydrogen embrittlement.

Work on these lines has been taken up at the National Metallurgical Laboratory to throw more light on the mechanism of cracking in different media. These studies will be carried out in the acid media, salt solution and marine and industrial atmosphere of Digha and Jamshedpur respectively.

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Notes and news

HOME NEWS

Technical Committee of raw materials preparation and improved iron production submits report

The Technical Committee set up by the Government of India sometimes back under the Chairmanship of Dr B. R. Nijhawn, Director, Hindustan Steel Limited and National Metallurgical Laboratory, to advise the Government on various steps towards raw-materials' preparation and technological improvements for improved iron production, has submitted its full Report to the Ministry of Steel. The Report is comprehensive and has discussed different parameters covering industrial production of pig iron under Indian conditions, relating for example, to indigenous raw-materials for iron smelting vis-a-vis current technological practices and the introduction of latest innovations and techniques, such as the use of super-basic self-fluxing sinter, pelletizing, injection of oil, light naphtha, high top pressure operations, optimum sizing of raw-materials for iron production and their economic beneficiation, high blast temperatures, oxygen enrichment of air blast, etc. The Report has highlighted the latest technological innovations employed in iron production in relation to the results obtained in overseas practices such as in the USSR, Japan, etc.

The Report has given an exceedingly rational and scientific appraisal of how far such latest specialized techniques and technological innovations can be implemented under Indian conditions with optimum economic advantages in relation to increased productivity, lowered production costs, quality of output, yield figures, etc. The Report has dwelt at length upon the main objectivity criteria of iron production under Indian conditions such as, attaining lowest possible coke rates in relation to maximum productivity, economics of iron production, quality of output and high yield etc. The Report has given the results of some of the latest trials conducted on laboratory, pilot plant and full industrial scale basis and their implications in relation to current iron smelting practices and techniques and employed in the country. Interalia other recommendations, the Committee has advocated certain specific short term and long range measures to effect significant improvements in iron production under Indian conditions, such as the urgency of optimum sizing of raw-materials and their economic beneficiation and subsequent agglomeration, the use of washed and dried coal for coking purposes, high blast temperatures in relation to superior stove refractories, oil injection, high top pressure blast furnace operations, etc. The Report has referred to the lead taken by the Tata Iron and Steel Works in the use of beneficiated raw-materials, oil injection in all their blast-furnaces, oxygen enrichment of air blast etc. on full production scale and in related fields in iron production. The Report has referred to the extensive and valuable research and pilot plant scale investigation trials on raw-materials preparation and agglomeration, including the production of super-basic self-fluxing sinter, pelletizing, conducted at the National Metallurgical Laboratory and at the TISCO Laboratories, etc. Some aspects of Australian iron production have been highlighted where high ash coke plagues iron smelting much the same way as is the case under Indian conditions.

Pig Iron Need

The Seven-Member Foundry Pig Iron Panel, constituted by the Union Government under the chairmanship of Mr K. Prosad is undertaking comprehensive tour of foundries of the country to study the requirements of pig iron to various foundries. The panel will make recommendations as to the type and quality of pig iron that should be allotted to the foundries, taking into account the character and quality of their finished products. The Panel will also recommend to the Centre short and long term measures to bridge the gap between supply and demand of foundry grade pig iron and is expected to submit its report to the Government by August 31st.

Special Steel Plant likely at Jamshedpur

An agreement between Tata Iron and Steel Co. and Kolee Steel Works and Nissho Trading Company, Japan, regarding the setting up of a special steel plant at Jamshedpur is expected to be finalised shortly. An integrated plant for the manufacture of alloy steel tools is proposed to be erected on the other side of the river Kharakai. The plant has an estimated capacity of 40 to 50 thousand tons. The plant will be commissioned after three years.

Indian Nation, 22.5.1965.

Aluminum Unit in Mysore

Mysore's single biggest unit in the private sector—the Rs 80 crore aluminium plant—will be located in Belgaum district. The plant with an initial capacity of 33 000 tons of aluminium a year, to be expanded in stages to 100 000 tons, is expected to go into production by the end of 1967 or early in 1968. Power for the plant will be supplied from the Sharawathi Project, the initial requirements being 75 000 kW. The plant, in the ultimate stage, will consume about one-third of the total power generated from the Sharawathi Project. Bauxite will be mined from the South Kolhapur district of Maharashtra as the Mysore State has very small deposits of not exceeding one million tons.

—Financial Express, 22.5.65.

Fourth Plan Estimate of Non-coking Coal Revised

The Ministry of Steel and Mines has revised the tentative target for production of non-coking coal in the Fourth Plan downwards, from 82·79 million tonnes to 79·29 million tonnes. The estimate for coking coal, however, remains the same as before—40 million tonnes excluding 5 million tonnes of blended coal. It has been estimated by the Ministry that the demand for coal in 1965-66 would be 67 million tonnes, including 17 million tonnes of coking coal and about 50 million tonnes of non-coking coal.

—Indian Express, 20.5.1965.

Crash Programme for Search of Minerals

A crash programme for mineral investigation called the 'Operation Hard Rock' is proposed to be launched after the monsoon this year in the Chotanagpur Plateau in Bihar, the Aravalli region in Rajasthan and the eastern party of Cuddapah Basin in Andhra Pradesh. Airborne surveys and latest geophysical techniques will be adopted in carrying out the investigations, which are expected to be completed in 30 months in the three mineral belts in the country. The operations will pinpoint favourably prospecting areas by areas by aeromagnetic and radiometric methods.

The primary objective of the programme is to find economic deposits of base metals such as copper, lead, zinc, etc. The 'Operation Hard Rock' will cost about Rs 2·15 cores out of which Rs 1·65 crore in foreign exchange will be met out of the 3·5 million dollars to be given by the USA as aid. The survey is being undertaken to step up investigations of minerals to keep pace with the tempo of industrialisation of the country. Presently India is spending more than Rs 45 crore in foreign exchange towards imports of non-ferrous metals like copper, zinc, lead, tin, nickel and aluminium.

—Indian Nation, 21.5.65.

OVERSEAS DIARY

World Tin Production Fell Short of Demand in 1964

The reason for the record prices attained on the tin metal markets of the world at the latter part of last year are amply explained by the latest figures published by the International Tin Council, which indicate that while world consumption of primary tin metal climbed by over 3·5 per cent, in 1964, smelter output was nearly one per cent lower. Production of tin in concentrates during the same period rose by an estimated 3·5 per cent. These estimates by the ITC which exclude the USSR, China and East Europe, showed that consumption of primary tin at 166 700 tons increased by 6 000 tons compared with the previous year. Output for the same period amounted to 142 800 tons against 143 100 tons, whilst production of tin concentrates increased by 5 600 tons to total 146 900 tons. This trend continued into 1965, when world consumption of primary tin metal during Feb. totalled 14 200 tons against 14 100 tons in January and 13 800 tons in February last year. Small rises were seen in the US and the UK where respectively 4 980 tons against 4 900 tons and 1 650 tons against 1 625 tons were consumed for February and January 1965 respectively.

Likewise in world smelter output of primary tin metal, lower production figures are given for February at 11 200 tons, against 12 700 tons in January and 10 500 tons in February, 1964. The fall was mainly due to a substantial loss in Malaysia, where output fall to 5 916 tons in February against 6 464 tons in the previous month. Production in the UK was practically unchanged in the first part of year at 1 697 tons in Jan. 1 681 tons in February and 1964 tons in March.

World output of tin-in concentrates declined in January this year to 12 200 tons compared with 12 500 tons in the previous month and 12 400 tons a year ago. Malaysia's production also fell during the first quarter of this year totalling 14 850 tons against 14 990 tons during the first quarter of 1964, despite the sharp increase in March to 5 271 tons against 4 169 tons in February.

The total reported and estimated stocks of tin-in-concentrates declined from 20 500 tons at the end of December, 1964 to 12 100 tons at the end of January, mainly due to a lower total in Malaysia where stocks fell to 3 175 tons at the end of January compared with 4 003 tons a month earlier. In February they declined further to 2 791 tons. The total reported and estimated commercial stocks of tin metal also declined from 49 500 tons a month a later, with defict mainly attributed to holdings in the US which fell to 20 685 tons at the January end against 21 265 tons in December. Stocks in Malaysia declined from 2 522 tons in January and 2 467 tons in February.

—Economics Times, 28.5.65.

Japan Iron and Steel Federation Survey

The growth of India's steel industry has been commented upon in a survey made by the Japan Iron and Steel Federation from 1954 to 1964, India's annual steel output increased 3·4 fold from 1 712 million tons to 5 197 million tons, the Federation says.

Making specific note of steel production in various countries it says that from the long term point of views, a re-distribution of percentages in world steel production appears inevitable. Other countries registering big advances include : Australia (from 2 232 000 to 4 900 000 tons), South Africa (from 1 431 000 tons to 2 994 000 tons), Brazil (from 1 148 000 to 2 903 000 tons), and Mexico (from 622 000 to 2 177 000 tons). As for Japan, the Japanese steel industry in 1964 produced some 40 million metric tons of steel, representing 9·2 per cent of the world's total production. In 1954, ten years earlier Japan accounted for 3·5 per cent of the world steel output.

The Federation says that of the major teel producing countries, apart from Japan, only Italy, India, Russia and a few nations of the communist block more than double their steel output during the past ten years. West Germany and France increased their production 1·8 times and Britain 1·4 times. The total world crude steel output in 1964 totalled 430 million tons an increased of about 46 million tons or 11·2 per cent, over the output in 1963.

From 1954 to 1964 the world steel production rose 92·4 per cent with all producing countries showing substantial gains. The US remained the world's largest producer, turning out 115 210 thousand tons of crude steel in 1964 against 80 118 000 tons in 1954. But its share of the total world production dropped from 35·4 per cent to 26·7 per cent. British production rose from 11 815 000 tons to 26 310 000 tons, but its world share declined from 8·4 to 6·1 per cent. West Germany turned out 20 239 000 tons in 1954 and increased it to 37 340 000 tons in 1964, though its world share shrunk from 9 to 8·8 per cent. The pattern in the French steel Industry was similar, with production showing an increase from 10 629 000 tons to 19 780 000 tons in 1964 with the percentage of its world total dipping slightly from 4·7 to 4·6 per cent.

—Economic Times, 27.5.65.

Pyrometallurgical Processes in Non-ferrous Metallurgy

'Pyrometallurgical Processes in Non-ferrous Metallurgy' will be a feature of the First Operating Metallurgy Conference in Pittsburgh at the Penn-Sheraton Hotel, November 29–December 3, 1965. The Conference will be held concurrently with the First Operating Metallurgy Exposition in the New Pittsburgh collseum. The meetings and exposition are sponsored by the Metallurgical Society, a constituent unit of the American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME).

Technical sessions of the Pyrometallurgy Symposium will be held on Monday, Tuesday, and Wednesday of the conference week. The two sessions on Monday, November 29, 1965, will be on a variety of process applications in non-ferrous metallurgy plants in North America, Europe, Africa and South America. Subjects will include blast furnace operation on nickel, copper and lead, reverberatory furnace practice, and converters. On Tuesday, November 30, there will be a session on modern roasting practice for zinc and copper, using fluid-bed and suspension techniques, and a second session on the production of by-product iron and steel in non-ferrous metallurgical plants. On Wednesday sessions are scheduled on the uses of bulk oxygen in non-ferrous metallurgical plants and a variety of subjects, including refractories, modern process instrumentation, and computer control of process.

The Four-day Symposium will conclude with plant trips to Joseph Town Zinc Smelter, St. Joseph Lead Company, Monaco, Pa., Hussey Metals Division, Copper Range Company Leetsdale, Pa., on Thursday, December 2. Other plant trips are being run simultanoeusly to Weshington, Pa., and Duquesne works, United States Steel Corporation, Duquesne, Pa.

—News release from the Metallurgical Society, New York.

Iron and Steel Plant in Yugoslavia

A new integrated Iron and Steel plant to be built at Simederovo, Yugoslavia, will be designed by a group of Leningrad engineers under a recently signed Yugoslav-Soviet contract. Specialising in flat rolled products, the new plant will provide sheet steel for motor cars, shipyard plate and plate for steam boiler factories. Initial output of crude steel will be 300 000 tons a year, but further development will increase this to one million tons, says a Belgrade report.

—The British Steelmaker, April 1965.

Blast furnace oxygen trials

The Appleby-Frodingham Steel Company branch of the United Steel Companies Ltd., UK, has revealed that oxygen is being used to increase the efficiency of the Queen Anne blast furnace. The oxygen is only 85 per cent pure and is of low pressure. The trials will last a month. The Queen Anne furnace has hearth diameter of 31 ft making it one of the largest furnace in the UK. It was constructed in 1954 with Queen Victoria furnace.

—British Steelmaker, April 1965.

Statistics

PRODUCTION OF PIG IRON, STEEL INGOTS AND SALEABLE STEEL

(Producer-wise)

(a) Blast furnace (hot metal)

(In thousand tonnes)

	1960-61		1961-62		1962-63		1963-64	
	Total	For sale	Total	For sale	Total	For sale	Total	For sale
Main producers								
Bhilai	722	382	1 000	375	1 170	341	1 296	408
Durgapur	404	255	728	282	1 056	391	1 302	418
Rourkela	389	167	434	67	732	81	829	98
Tisco	1 588	6	1 648	25	1 789	14	1 812	6
Iisco	1 161	229	1 187	235	1 292	239	1 237	203
Mysore	64	12	59	8	78	—	85	—
Total	4 325	1 051	5 057	992	6 117	1 066	6 561	1 133
Secondary producers								
Kalinga industries	26	26	26	30	30	28	22	22
Acme	—	—	—	—	4	4	9	9
Grand Total	4 351	1 077	5 087	1 022	6 149	1 098	6 592	1 164

(b) Steel ingots (Total) and Steel ingots (Elec. Fces.)

(In thousand tonnes)

	Steel ingots (Total)				Steel ingots (Elec. Fces.)			
	1960-61	'61-62	'62-63	'63-64	1960-61	'61-62	'62-63	'63-64
Main producers								
Bhilai	401	789	1 060	1 143	—	—	—	—
Durgapur	169	462	731	972	—	—	—	—
Rourkela	212	354	702	800	—	—	—	—
Tisco	1 626	1 625	1 798	1 892	15	13	16	18
Iisco	914	934	1 002	1 027	—	—	—	—
Mysore	51	49	46	48	2	3	2	2
Total	3 373	4 213	5 339	5 882	17	16	18	20
Secondary producers								
Bhatia Electric Steel Co.	—	—	4	2	—	—	4	2
National Iron & Steel Co.	—	—	16	15	—	—	16	15
G. K. W. Ltd.	—	—	14	16	—	—	14	16
Mukund Iron & Steel Co.	—	—	7	7	—	—	7	7
J. K. Iron & Steel Co.	—	—	9	10	—	—	10	9
Hindustan Iron & Steel Co.	—	—	4	2	—	—	2	4
Steel Rolling Mills of Hindustan Ltd.	—	—	—	—	—	—	—	6
Total	55	54	56	63	55	54	56	63
Grand Total *(Main producers & Secondary producers)*	3 428	4 267	5 393	5945	72	70	74	83

(c) Semi-finished Steel for sale

(In thousand tonnes)

	1960-61	1961-62	1962-63	1963-64
Bhilai	309	178	244	220
Durgapur	119	290	265	349
Rourkela	73	10	4	2
Tisco	391	395	431	472
Iisco	220	163	160	176
Total	1 112	1 036	1 212	1 219

From statistics for Iron and Steel Industry in India—*Published by HSL.*

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VOLUME VII **NUMBER 3** **AUGUST 196**

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1966

NML Symposium on

Metallurgy

of

Substitute Ferrous & Non-Ferrous Alloys

The scope of the Symposium will cover the following:

1. **Theoretical principles of substitution of ferrous and non-ferrous metals and alloys in relation to metallurgical characteristics and physical properties of end products.**

2. **Development of substitute ferrous and non-ferrous alloys in general in different countries in times of peace and emergencies including requirements of stock-piling.**

3. **Development of ferrous and non-ferrous substitute alloys under Indian raw-materials' conditions and market requirements.**

4. **Practical aspects of substitution of ferrous and non-ferrous metals in relation to industrial production and fabrication parameters.**

5. **Special purposes substitute alloys developed for specific applications, such as for light armour, aluminium alloy cartridge cases, substitute stainless and high speed steels, etc.**

6. **Study of economics of substitution of ferrous and non-ferrous metals under Indian conditions in the background of world conditions in general.**

7. **Standard specifications for substitute ferrous and non-ferrous alloys.**

Invitations are being extended to technologists, metallurgists and research scientists at home and abroad to attend the Symposium in person and contribute technical papers for discussion.

NML TECHNICAL JOURNAL

Vol. VII No. 3 AUGUST 1965

Substitute Alloys

IN the wake of depleting mineral reserves and their shortages and, in certain cases, in the almost total absence of some, researches and applied technological efforts are directed towards mineral conservation on the one hand and making the maximum optimum use of available resources on the the other. In doing so, unconventional uses have to be made of different metals and their alloys through the judicious development of 'Substitute' ferrous and non-ferrous families of alloy compositions. The subject of substitute alloys has always tended to be somewhat controversial adjudged on the basis of indigenous availability of the primary metals not only in relation to metallurgical acceptability of the substitute alloys but also *vis-a-vis* their production economics, consumer acceptance and serviceability. The scope of research in such a field would be vast indeed even in its reference to diverse metallurgical alloys, wherein such substitution could successfully be introduced in times of both peace and war emergencies ; in either case, the scope of potential substitution will cover a wide spectrum. As such, the diverse substitutional factors have to be rationally and scientifically examined to establish their industrial scale implementation, particularly in the context of Indian conditions.

Metals in which our country, whilst possessing some resources, is highly deficient are copper, zinc and lead. The metals in which we are potentially rich are iron, aluminium, titanium, magnesium, beryllium, manganese, etc. Metals such as nickel, tin, molybdenum, tungsten either do not exist or are perhaps found in isolated uneconomic pockets, even though with more intensified and comprehensive exploration and prospecting some economic deposits thereof may yet be discovered.

The very vast technical literature on the subject of Metallurgy of Substitute Ferrous and Non-Ferrous Alloys, though rich in its technical wealth, presents a diffused array of dispersed and scattered references set loose in technical journals, text books and in a formidable number of world patents which multiply in the field today.

The National Metallurgical Laboratory has chosen this subject for its next Symposium not because many are not fully conversant with different facets of this important and vast subject but more so, for cataloguing and focussing attention on known families of substitute alloys in relation to others offering potential scope to engineers and metallurgists alike.

With a view to focussing attention on multitudinous aspects of 'Metallurgy of Substitute Ferrous and Non-Ferrous Alloys' a Symposium is being organised by the National Metallurgical Laboratory in early 1966, which will provide an international forum to discuss the subject, wherein metallurgists, engineers, research workers, industrialists, consumers and planners can get together and exchange technical 'know-how', examine inter-related problems and facilitate further research studies on the subject.

Determination of Nitrogen in Solid Solution in Steel by Electro-Chemical Method

A. N. Chatterjee
N. G. Banerjee
T. Banerjee

The authors studied the electro-chemical method for determining nitrogen which is in solid solution in steel. When a steel sample is anodically dissolved in sodium potassium tartrate and sodium chloride solution, the metal crystals break down liberating the atomic nitrogen which escapes as gas. Samples of plain carbon steels and low alloy steels were anodically dissolved and the gases liberated were collected and analysed for nitrogen. Reproducible values for nitrogen were obtained with plain carbon and low alloy steels.

A small portion of the total nitrogen contained in ferrous metals and alloys is in solid solution. This nitrogen may precipitate during ageing and thus control physical and mechanical properties of the metals and alloys. Austenitic structures of steels are stabilised by nitrogen in solid solution.

An accurate determination of soluble nitrogen in alloy steel is till now a difficult problem. The best values of solubility in equilibrium with Fe_4N are those of Dijkstra[1] deduced from the measurements of the internal friction of nitrogen containing alpha-iron and those of Borelius[2] and his collaborators based on their method of isothermal calorimetry. The recent work of Fast and Verrijp[3] established that the internal friction of fine grained textureless alpha-iron wires caused by nitrogen is proportional to the nitrogen content up to concentration corresponding to its solubility at the eutectoid temperature (0·95 % by wt. at 585°C). They determined the solubility of nitrogen in equilibrium with Fe_4N at different temperatures by the internal friction method. At 20°C, the solubility has been found to be $1{\cdot}48 \times 10^{-5}\%$ by weight. But the estimation of soluble nitrogen in alloy steel, specially where solubility is very high, is difficult by internal friction measurement method as stated by G. M. Leak[4] in his recent paper.

The indirect method of determining the soluble nitrogen is based on finding the difference of total nitrogen estimated either by the Kjeldahl or vacuum fusion method and the values of nitride nitrogen estimated either by chemical or X-ray analysis method. The following chemical methods are generally adopted for the estimation of nitrogen contained in the nitride :

(i) *Beeghly method:*[5] The method consists in dissolving the iron matrix by methyl acetate and bromine and separating the nitrides from the matrix. The nitrides are then washed with methyl alcohol and digested in sulphuric acid and nitrogen is determined by the Kjeldahl method.

(ii) *Ammonium persulphate method:* Another method of estimating nitrogen contained in nitrides has been discussed by R. E. Fryxell et al.[6] It involves estimation of the different forms of nitrogen existing in 3% silicon-iron alloy. They dissolved the sample in 10% ammonium persulphate at a temperature of 45°C under stirring. The reaction was completed in two hours. The silicon nitride which is insoluble in aqueous solution of ammonium persulphate was identified by X-ray diffraction method.

Except the physical method i.e. the internal friction method, no other method for the direct determination of nitrogen in solid solution in steel or in ferro-alloys has been practised till now. Recently Yu. A. Klyachko and O. D. Larina,[7] while describing the electro-chemical method for the determination of hydrogen in steel, indicated the possibility of determination of the part of the nitrogen in steel which remains in solid solution by the electro-chemical method. They suggested that when a steel sample is subjected to anodic solution, the metal crystal lattice breaks down and the atoms of the gaseous elements present in a solution are freed and liberated. For this purpose, the anode potential should be so regulated that no gassing due to the decomposition of the electrolyte occurs at the anode surface. The pH of the electrolyte should be so regulated that no chemical corrosion takes place, so that nitrogen value may not be less due to possible formation of ammonia. Moreover, the hydrogen liberated at the cathode should not be allowed to come to the vicinity of the anode to contaminate the gases there.

On fulfilment of the above conditions, according to Klyachko and Larina, decrystallization of the anode proceeds with the passage of electric current and liberates that part of nitrogen present in the form of interstitial solid solution. The hydrogen which is either in molecular or atomic form in the specimen also gets liberated and is collected over the anodic chamber.

Messrs A. N. Chatterjee, Senior Scientific Assistant, N. G. Banerjee Scientist, and Dr T. Banerjee, Scientist, National Metallurgical Laboratory, Jamshedpur.

An apparatus, shown in Fig. 1, was designed and fabricated for the determination of gases in metals by anodic dissolution. The electrolytic cell consisted of two one litre beakers, connected at a height of 20 mm from the bottom by a ground glass joint 40 mm wide. Inside the joint was a flange to which was fixed a membrane of double filter paper which was pressed tightly so that no electrolyte could leak out of the vessel. The filter papers worked as diaphragms and prevented free exchange of liquids between the beakers. Thus, hydrogen from the cathode chamber got less chance to be carried over to the anode chamber. One inverted graduated burette ending with a V-shaped funnel at the bottom was placed over the sample constituting the anode. At the top of the burette, one 3-way stop cock was attached through which the collected gas could be introduced into the Ambler's gas analysis apparatus for the final analysis. A platinum foil was used as a cathode. The sample forming the anode was connected to a 2·32 mm dia. platinum wire which passed through a rubber cork fitted to the funnel of the burette.

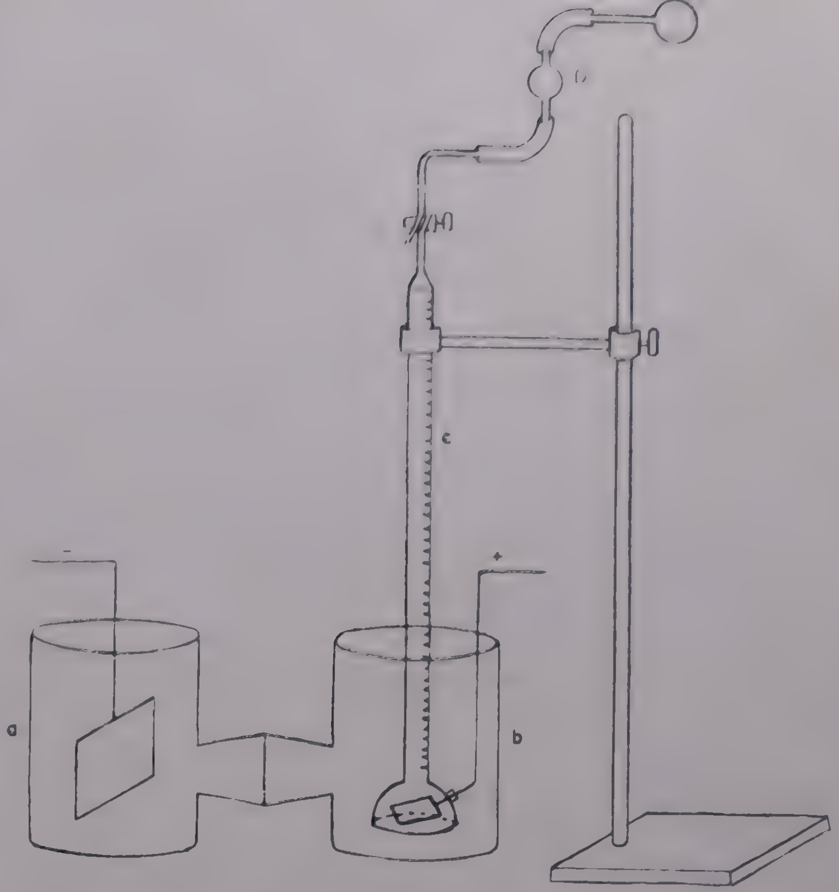
Electrolyte used

The electrolyte used contained 25 gm of sodium potassium tartrate and 150 gm of sodium chloride per litre at a pH of 6–6·6. Sodium chloride helped the anodic dissolution and sodium potassium tartrate acted as a buffer and at the same time formed a soluble complex salt with iron. Electrolysis was done at a current density of 0·3–0·5 amp/sq cm. Change of temperature of the catholyte and anolyte was recorded and kept within 30–35°C.

Observations

The size of the specimen was varied with the nitrogen content and usually 1″×½″×½″. Samples of plain carbon steels and alloy steels of different compositions were anodically dissolved for the estimation of nitrogen in solid solution. Reproducible results were obtained as given in Table I.

During the anodic dissolution, gas evolved was collected in the inverted burette as in Fig. 1. The gas was then led into the Ambler's gas analysis apparatus where the gases were analysed for nitrogen and hydrogen. Hydrogen was determined by burning it with excess of oxygen and nitrogen was estimated by the difference. During the analysis, few samples showed high hydrogen value in comparison with vacuum heating method. Specially in the case of heat treated stainless steel samples (heat treated for precipitation), hydrogen content recorded by this method was higher than that obtained by vacuum heating method. Nitrogen values obtained by this method were compared with the values obtained from the total nitrogen and nitride nitrogen. Total nitrogen was determined by vacuum fusion method and the nitride nitrogen was estimated from the anode slime and from the electrolyte by Kjeldahl method.



1 Apparatus for determination of gases in metals by anode solution.

When attempts were made to dissolve anodically samples of austenitic nickel-free stainless steels (solution treated) all of them showed extreme passivity instead of anodic dissolution. Composition of the nickel-free stainless steel was Cr 17–23%, N_2 0·6–1%, Mn 14–17%. The passivity observed may be due to high chromium in the alloy.

TABLE I Estimation of nitrogen and hydrogen by electro-chemical method.

Sample	C.D. amp/cm^2	% of solid soluble N_2 by wt. by electrolytic method	Total N_2% by vacuum fusion method	Nitride N_2 %	H_2 in cc per 100 gm by electrolytic method	H_2 in cc per 100 gm by vacuum heating method
Nitrided steel (0·85% Mn)	0·33	0·008	0·036	0·027	1·6	1·5
Nitrided steel (0·91% Mn)	0·30	0·007	0·029	0·022	1·8	1·67
Nitrided steel (1·1% Mn)	0·36	0·0084	0·038	0·088	2·1	2·1
Low alloy steel (0·62% Cr)	0·42	0·002	0·012	0·0105	1·9	1·8
Low alloy steel (0·85% Cr)	0·38	0·0024	0·014	0·013	1·8	1·85
Medium Mn rail steel	0·37	0·0022	0·009	0·0066	1·6	1·55
18 : 8 stainless steel	0·51	0·0054	0·026	0·0203	6·0	4·2
Ni-free stainless steel B_1 (heat treated for 1 000 hours at 600 C)	0·42	0·060	1·01	0·93	7·0	3·5
Ni-free stainless steel B_2 (heat treated for 1 000 hours at 700 C)	0·46	0·041	0·68	0·636	9·0	4·2
Ni-free stainless steel B_3 (heat treated for 1 000 hours at 800 C)	0·47	0·032	0·98	0·942	11·00	4.6

Due to abnormally high hydrogen value obtained from the anodic dissolution of the nickel-free stainless steel, it was considered necessary to check the hydrogen value of the plain carbon steel. Klyachko and O. D. Larina[7] claim to have determined hydrogen in steel accurately by the electrolytic method. Klyachko and Larina[8] claim also to have estimated separately the molecular and atomic hydrogen in steel by the anodic dissolution method.

To repeat their experiment, the same type of the bath and condition was adopted. A mild steel sheet was cut to the size $2'' \times \frac{3}{8}'' \times \frac{1}{8}''$ with a notch in the middle. When the mild steel samples as received were analysed both by electrolytic method and by vacuum heating method, the hydrogen values were in agreement. The sample was cathodically charged with hydrogen for a reasonable time so that at least 10–15 cc hydrogen per 100 gm might be absorbed. The sample was then taken out from the charging bath and broken at the notch; one portion was anodically dissolved and the other put in the vacuum heating furnace to estimate total hydrogen content of the sample. Hydrogen impregnation by the above method was found to be very efficient, because both the pieces of the sample were found to pick up hydrogen in equal quantity. But when both the pieces were analysed, one by anodic dissolution and the other by vacuum heating method, the results were found to vary appreciably, as shown in Table II.

TABLE II Comparison of hydrogen values obtained by electro-chemical method and vacuum heating method.

Sample	Mode of charging	H_2 in cc/100 gm by V.H. method	H_2 in cc/100 gm by electro-chemical method
Mild steel plate	Without charging	1·11	1·30
,,	,,	1·30	1·40
,,	,,	1·20	1·21
,,	,,	1·02	1·10
,,	Thermal charging at temp. 1 100°C	3·90	3·80
,,	,,	4·20	4·30
,,	,,	4·10	4·05
,,	Cathodic charging at C.D. 1·2 amp/cm²	14·4	11·55
,,	,,	9·1	6·20
,,	,,	11·5	8·10
,,	,,	7·1	4·9

The hydrogen values have also been determined by both the methods in mild steel after thermal charging of hydrogen. In this case, hydrogen values by both the methods were found to be in agreement. But when the sample was cathodically charged, the hydrogen value obtained by the vacuum heating method was higher than that by the electrolytic method. The lower values of hydrogen obtained by the electro-chemical method when the sample was cathodically charged, may be considered from the assumption made by Klyachko and Larina[8] molecules were also entrapped into the matrix along with hydrogen. These water molecules may account for high hydrogen value in the vacuum method but not so in the electrolytic method.

From the experimental data, it is evident that the accuracy of the analysis by electro-chemical method of both hydrogen and nitrogen depends on certain factors.

Solubility of nitrogen in the electrolyte does not affect the nitrogen value as its solubility is very low and decreases with the increase of NaCl concentration in the solution. In the present investigation, 15% NaCl solution has been used, the temperature of which was 30°C–35°C, where the solubility of nitrogen in the electrolyte is quite negligible. According to Christoff and Braun,[9] solubility of nitrogen in sodium chloride solution is shown as follows:

		5°C	10°C	15°C	20°C	25°C
NaCl	0·6%	0·020%	0·0185%	0·0164%	0·0148%	0·013%
	11·73%	0·0102%	0·0093%	0·0081%	0·0066%	0·0047%

Conclusion

Both the values of hydrogen and nitrogen in mild steel and low alloy steel were reproducible. Hydrogen value obtained by the electro-chemical method was quite comparable with that obtained by the vacuum heating method. The nitrogen values obtained by electrolytic method when compared with the values obtained for total nitrogen and nitrogen contained in the nitrides were also quite in agreement. This method of estimation of nitrogen in solid solution is quite satisfactory when applied to plain carbon steel and low alloy steel. But some more study is yet necessary to introduce this method for the determination of interstitial nitrogen in some special alloy steels.

Acknowledgement

The authors wish to thank Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, for his keen interest in this investigation and permission to publish this paper.

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Some Laboratory-Scale Trials on Electro-Slag Melting

R. D. Gupta
P. K. Gupte
B. R. Nijhawan

Electro-slag melting studies were made on the change in chemical composition, inclusion type and content and ingot structure of plain carbon, ball bearing and high speed steels. It was found that sulphur and inclusion content could be reduced up to 70 per cent, silicate and sulphides were reduced to the minimum and the cast ingot structure was freel from axial porosity and segregation. In the case of high speed steels, carbides were evenly distributed.

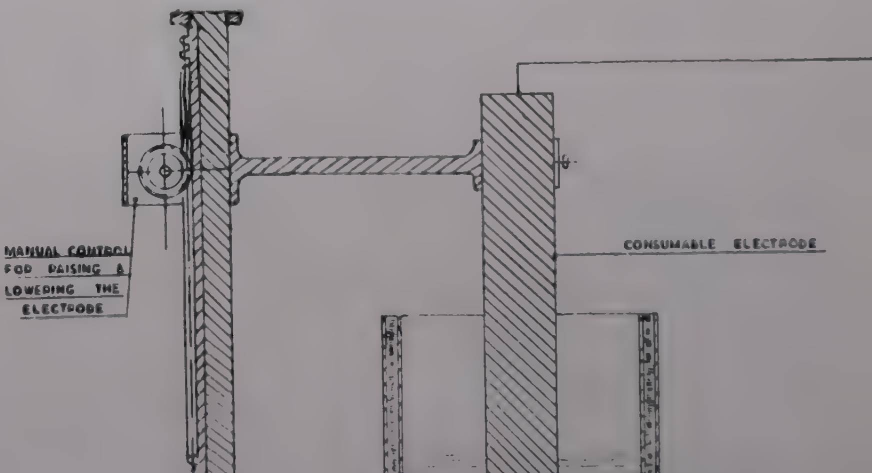
MODERN techniques such as vacuum stream degassing, vacuum melting and casting, consumable electrode vacuum arc melting and electro-slag remelting are employed in steel refining to achieve super-clean and pure alloys having a minimum of unwanted gaseous impurities. All these processes except electro-slag remelting require high capital investment. Electro-slag melting is employed industrially in advanced countries for the production of alloys, such as ball bearing steels, heat resistant alloys, stainless steels, etc. The simplicity and the ease of operation of this process have aroused great interest in the metallurgical field.

For making quality steels, the use of acid open hearth furnace is very well known. But the use of the process is limited due to the non-availability and expensive nature of the low sulphur and phosphorus steel scrap employed. In order to make up for the cost of scrap, the basic electric arc furnace was employed, where commercial steel scrap could be used taking advantage of the refining potential of the process with respect to sulphur and phosphorus. But the basic oxide slag made in the process leaves room for residual oxides in the steels, and also hydrogen pick-up from the atmosphere.

Vacuum degassing is normally carried out under a pressure of 1 mm – 4 mm of Hg. The requirements of certain engineering components subjected to heavy vibrations and fluctuating stresses need the alloy steels with very low inclusion contents. In order to meet the above requirements, use of the vapour pressure of the oxide has been made, and the steels are melted under such vacuum wherein most of the oxides dissociate. Dissociation is accelerated by the presence of carbon in the alloy which even in minute proportions is very effective.

Russians have developed the process of 'electro-slag remelting'' very much similar to consumable electrode vacuum arc melting. In both cases, conventionally made steels are refined during remelting—in the former case by refining through a synthetic slag and in the latter by extraction and elimination of gases under high vacuum. The process is extensively employed in U. S. S. R. on industrial scale for the manufacture of high quality alloy steel to meet very stringent specifications.

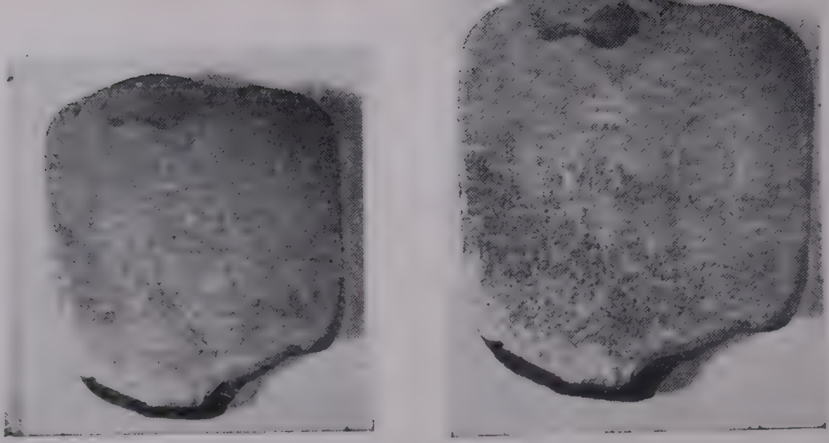
For vacuum melting, India will have to depend for years on the import of the entire vacuum equipment needed in vacuum induction melting as also for consumable electrode arc melting, while in the process of



1 *Schematic diagram of electro-slag remelting set-up.*

Messrs R. D. Gupta, Scientist, P. K. Gupte, Scientist and Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, Jamshedpur.

2 *Actual set-up used in electro-slag remelting experiments.*



×1 ×1½

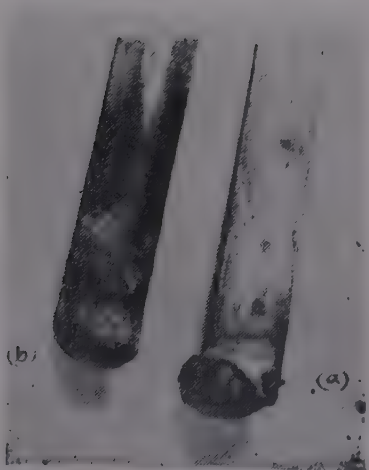
5 *Longitudinal section of electro-slag remelting (steel —0·40%C) Macroetched 50% HCl.*

electro-slag remelting, no vacuum equipment is needed. The need of low voltage transformers, voltage stabilisers and automatic electrode regulation can well be met indigenously. A project was taken up at the National Metallurgical Laboratory to develop the detailed technical know-how of the process especially suited to Indian conditions.

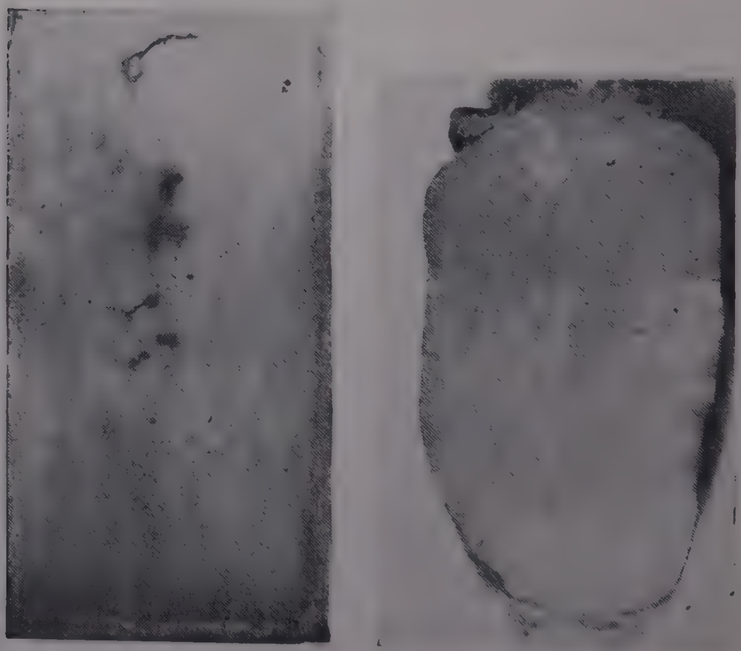
Electro-slag Process

Basically the electro-slag process consists in melting and refining through a synthetic slag. The only investment in this process is a suitable low voltage transformer. For our experimental work, a single phase 24 kW transformer was employed. For industrial applications, single phase as well as three-phase transformers have been used ; in the latter case three ingots can be cast at the same time. Voltage stabilizers regulate the movement of the electrodes in order to give a regular and uniform operation of the process. During the process of melting, the temperature of the slag is of the order of 1 700–1 900°C which results in the melting of the electrode and metal dripping through the slag in the form of

3 *Electro-slag remelted ingot* ×1

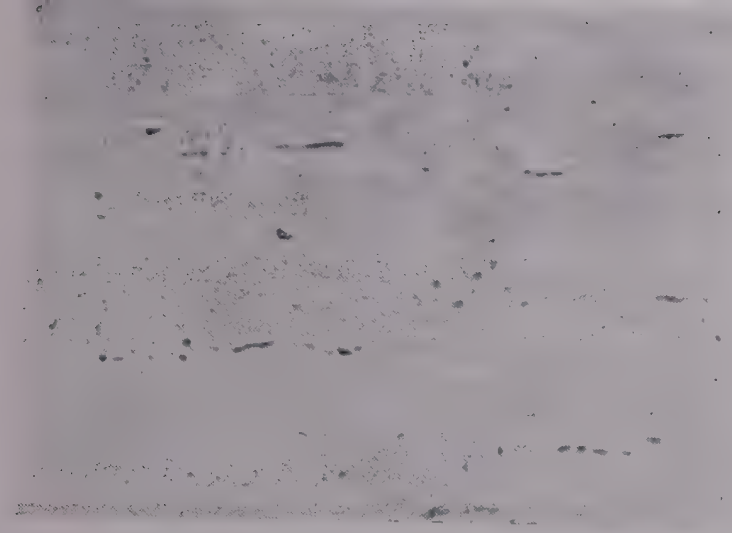


4 *Unconsumed ends of two electrodes at the end of remelting*



(*a*) *High frequency melt.* (*b*) *Electro-slag remelt.*

6 *Longitudnal sections of cast ingots of high speed steel (18 : 4 : 1) Macroetched 50% HCl.* ×1



(*a*) *Electric arc furnace melt* ×*150*

(*b*) *Electro-slag remelt* ×*150*

7 *Microphotographs of forged E.F. 36 (Medium carbon arc furnace heat) before and after electro-slag remelting.* *Unetched.*

droplets whereby it gets refined. Sulphur contents are thereby reduced by 30–60% (depending on the initial sulphur contents) and the non-metallic inclusions in the remelted products are few and more so are present in the form of harmless fine-globules.[1] The cast surface is superior and smooth in the absence of metal-mould reaction due to the slag layer on the mould wall. During the process, melting and solidification proceed simultaneously and no axial porosity and segregation is visible in the electro-slag refined ingots.

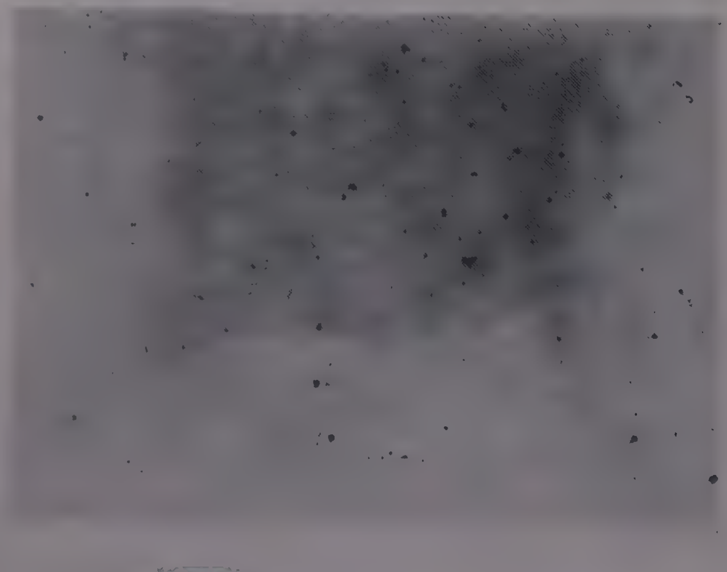
Both square and round mild steel ingot moulds can be used. The ingot mould forms one terminal of the output line from the transformer and electrode the other. In order to initiate the reaction, a small quantity of self-fusing flux containing Al-Mg alloy and KNO_3 is used. The flux produces the initial molten slag on initial electric arcing which ultimately forms an electrically conducting media for the current to flow between electrode and the mould bottom. Due to the resistance offered by the slag to the electric current flow, the slag attains very high temperature (about 1 900°C) which helps in the melting of the electrode. Calcium fluoride forms a major proportion of the working flux in order to impart electrically conducting property thereby. Such mixtures normally contain 70% of calcium fluoride and 30% alumina or, in some cases, part of the alumina is replaced by other constituents, such as lime, according to the refinement required. In order to prevent the sticking of the remelted ingot to the mould bottom, a mild steel pad is used in the bottom of the ingot which forms the first arcing base and thus normally gets welded with the ingot bottom.

The working flux mainly comprises of calcium fluoride (fluorspar) and alumina. For experimental trials acid grade fluorspar beneficiated at the National Metallurgical Laboratory from indigenous fluorspar and high grade alumina (more than 99% purity) manufactured by Indian Aluminium Co., Muri were employed. Alumina needed calcination for dehydration before use. The approximate chemical composition of acid grade fluorspar (ISI standards) is as follows :

CaF_2	... 97%
$CaCO_3$	... 1–2%
SiO_2	... 1%
Mixed oxides	... 0·1–0·5%

A schematic diagram of electro-slag remelting set-up is shown in Fig. 1. Figure 2 shows the set-up used for doing experimental trials at the National Metallurgical Laboratory. The feeding of the electrode is done manually with the help of a pulley. A mild steel closed

(*a*) *Electric arc furnace melt* ×*150*



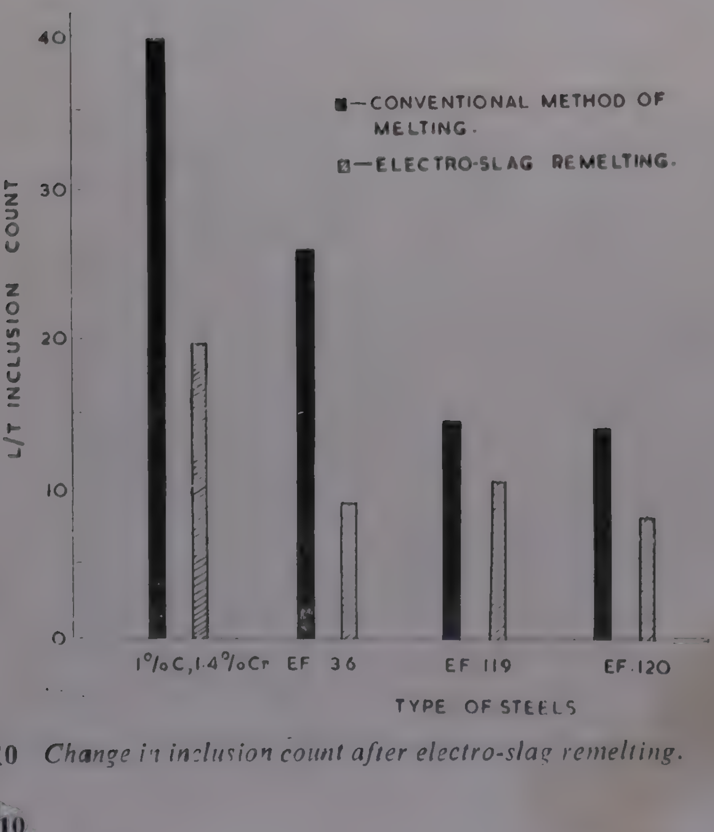
(*b*) *Electro-slag remelt* ×*150*

8 *Microphotographs of forged E. F. 119 (Medium carbon arc furnace heat) before and after electro-slag remelting. Unetched.*

(*a*) *High frequency melt* ×*150*

(*b*) *Electro-slag remelt* ×*150*

9 *Microphotographs of forged 1%C. 1·4%Cr steel (High frequency melt) before and after electro-slag remelting.* *Unetched.*



10 *Change in inclusion count after electro-slag remelting.*

bottom cylindrical ingot mould of 2″ inside and 1/4″ wall thickness has been used for all the experiments. Mould walls are cooled by a circular water spraying ring along the mould wall as shown in Fig. 2. A 24 kW A.C. welding transformer with two output voltages of 80 and 100 volts and various current settings to the maximum of 300 amp has been used for the work. During experimental trials, the transformer setting was kept constant viz. 80 volts and 300 amp. An ammeter is connected with the line to regulate the feed of the electrode.

Electrode was lowered whilst in contact with the steel pad, 100 gm of ignition flux and 150 gm of working flux were added respectively in the mould. Water circulation was checked. The main switch of the transformer was switched on and simultaneously the electrode was raised a little to initiate the arc to fuse the flux thus starting the process of electro-slag remelting. An attempt was made to keep the working current about 200 amp. Further additions of flux were made as and when necessary; when the electrode was almost consumed, the current was switched off and the residual electrode was withdrawn. Insufficient molten flux may give rise to build-up on the top of the ingot surface. Figure 3 shows an electro-slag remelted ingot and Fig. 4 shows the unconsumed ends of the two electrodes. End (a) indicates either the total absence of slag or the presence of a very thin layer of molten slag cover on the remelted material while (b), a clean end, is an indication of a regular molten slag cover all through the experiment.

Due to manual control, the feeding rate could not be kept uniform thus resulting in frequent "make and break" contacts, which resulted in prolonging somewhat the refining time whilst automatic control would provide speed in refining cycles. The maximum weight of the cylindrical cast ingot of 1–7/8″ diameter was 1 160 gm. Electrodes up to 5/8″ diameter and 5/8″ square cross sections were used during the experiments. Working flux of composition 70 : 30 (CaF_2 and Al_2O_3) was employed in all the experiments.

Experimental results

Some steels manufactured in 1 ton basic electric arc furnace and 25 lb high frequency furnace at the National Metallurgical Laboratory were forged and rolled to 5/8″ square cross section or 5/8″ dia. rounds. Chemical analyses of the various electrodes and their remelted ingots are given in Table I.

The surface finish of the electro-slag refined steel ingot is highly smooth due to the absence of any metal mould reaction and because of the intermediate layer of slag formed in the water cooled mould walls. Surface finish of one of the cast buttons is shown in Fig. 3.

In order to compare the solidification characteristics of the electro-slag remelted cast ingot and the conventional ingots cast in C.I. moulds, one ingot of each type was longitudnally sectioned, their sections were polished and macroetched with 50% HCl. The typical macrophotograph of a medium carbon steel ingot and high speed steel ingot before and after electro-slag remelt are shown in Figs. 5 and 6.

Study was made of the inclusion contents, their types and distribution for these steels. Some sets of specimens were prepared from 5/8″ sq. bars in each case. Microphotographs were taken to study the distribution and type of inclusions and are shown in Figs. 7, 8 and 9.

TABLE I Chemical analyses of steels used and their final analyses after electro-slag remelting (percentages)

Steel sample	Electrode C	S	P	Si	Mn	W	Cr	V	Al	Electro-slag remelt from the electrode C	S	P	Si	Mn	W	Cr	V	Al	Percentage reduction of 'S'
Commercial mild steel	0·22	0·02	0·03	0·09	0·69	—	—	—	0·01	0·23	0·006	0·03	0·12	0·64	—	—	—	0·1	70
E F 36	0·44	0·016	0·028	0·47	0·77	—	—	—	Tr	0·39	0·005	0·028	0·47	0·77	—	—	—	Tr	70
E F 119	0·45	0·009	0·027	0·37	0·94	—	—	—	Tr	0·44	0·006	0·027	0·47	0·84	—	—	—	Tr	33
E F 120	0·61	0·01	0·029	0·29	0·81	—	—	—	Tr	0·59	Tr	0·03	0·54	0·74	—	—	—	Tr	
HF 505 1% C, 1·4% Cr, Ball-bearing steel	0·98	0·04	0·02	0·46	1·02	—	1·30	—	—	0·95	0·01	0·04	0 43	0·98	—	1·27	—	0·20	75
HF 520 18/4 1 High speed steel	0·7	0·009	0·008	0·32	0·37	18·25	4·4	1·28	—	0·7	Tr	0·012	0·24	0·26	18·25	4·12	1·28	—	

The microphotographs (Figs. 7, 8, 9) depict the inclusion contents whilst numerical inclusion counts were also undertaken. The inclusion count method L/T (Lineal – Traverse) based on the work of G.K.N. Research Group Laboratories[2] was used in this investigation. The L/T counts of various sets of experimental steels are given in Table II and have been graphically represented in Fig. 10. In case of 1% C, 1·4% Cr ball-bearing steel the inclusion study was also made by A.S.T.M. standards E 45-51 of inclusion count. After comparing with the J. K. Chart, 25 fields were examined in each sample and the average counts are given in Table III.

TABLE II Comparison of inclusions count (L/T 'Lineal Traverse' count method) of the steels made by electric arc and high frequency method and electro-slag remelting.

Steel		L/T count (Inclusions/cm)	% Reduction in inclusion count
Arc furnace	EF 36	25·4	64
ESR	EF 36	9·08	
Arc furnace	EF 119	14·2	24·7
ESR	EF 119	10·7	
Arc furnace	EF 120	14·1	44
ESR	EF 120	7·9	
High frequency 1% C, 1·4% Cr.	HF 505	40·0	52
ESR ,,	HF 505	19·2	

TABLE III Inclusion study of ball-bearing steel based on J. K. Chart (A.S.T.M. Standards E 45-51)

Sample H. F. 505	A Sulphide T	H	B Alumina T	H	C Silicate T	H	D Globular oxide T	H
High frequency melt.	0·38	0·65	0 50	0·16	nil	0·24	0·80	1·34
Electro-slag melt.	Nil	Nil	0·54	0·40	nil	nil	1·50	0·92

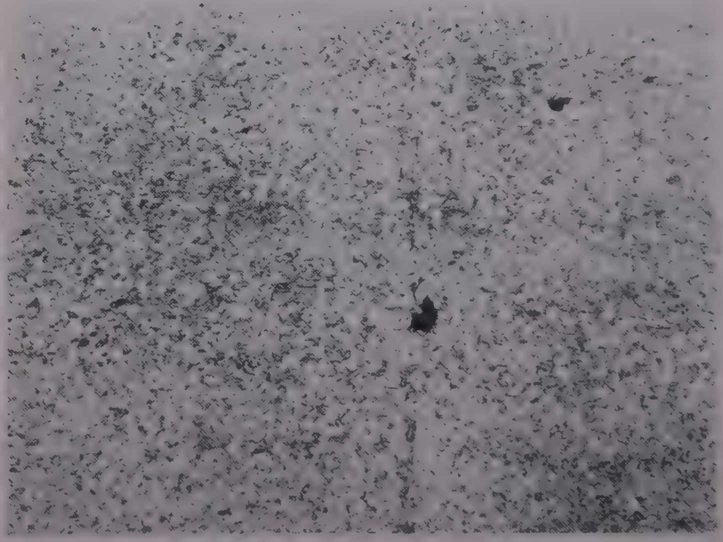
T = Thin
H = Heavy

The end products – 5/8″ sq. bars of ball bearing steel (1% C, 1·4% Cr steel)—manufactured by high frequency furnance and by electro-slag remelting were analysed for gaseous content by the vacuum fusion gas analysis method. The results are given in Table IV.

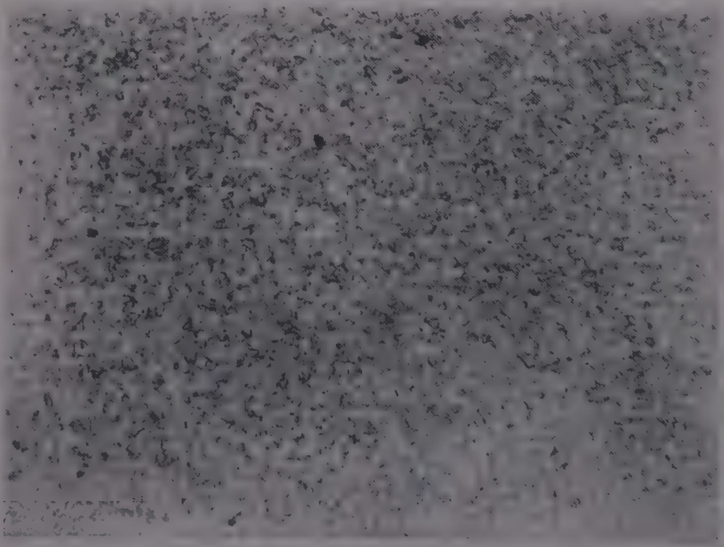
In order to study the segregation effect, the electro-slag remelting of high speed steel was also investigated. One heat of 18 : 4 : 1 type high speed steel was made

TABLE IV Gaseous content of 1% C, 1·4% Cr steel before and after electro-slag remelting.

Sample	Element	%Composition of gases Electrode prior to melt	After electro-slag remelting	% Reduction
H.F 505	Oxygen	0·0088	0·0070	+20·5%
	Nitrogen	0·0050	0·0053	— 6·0%
	Hydrogen	0·000114	0·000095	+13·5%

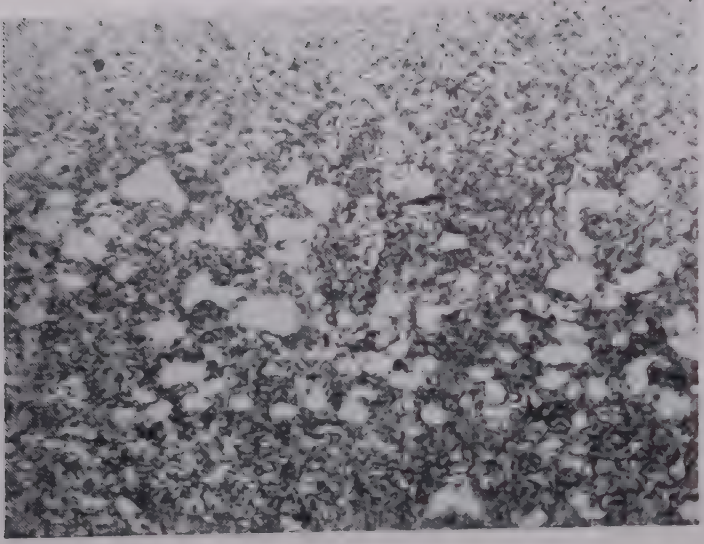


(a) High frequency melt *(Hot worked 87·9%)*
Etchant—Nital *×150*



(b) Electro-slag remelt *(Hot worked –85·9)*
Etchant—Nital *×150*

11 *Microphotographs of 18 : 4 : 1 high speed steel before and after electro-slag remelting—showing carbide distribution.*



(*a*) *High frequency melt* ×570

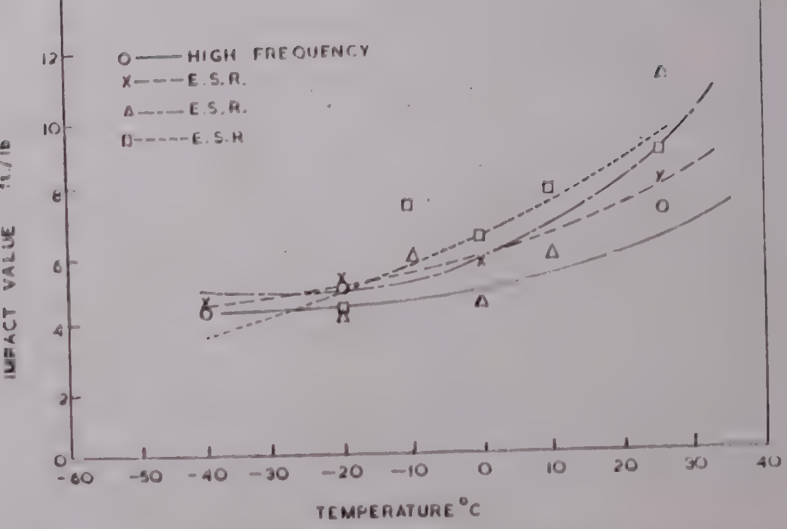
(*b*) *Electro-slag remelt* ×570

12 *Microphotographs of 18 : 4 : 1 high speed steel samples (same as in Fig. 11) showing the difference in the shape and distributions of carbide at higher magnification.*

in a 25 lb high frequency furnace and cast into 2″ sq. moulds. One of the ingots was forged into 5/8″ sq. bars and electro-slag remelted. The electro-slag remelted ingot was also forged to 5/8″ sq. bar and the cross sections of 5/8″ sq. bars of both types of steel were polished and microphotographs showing carbide distribution are shown in Figs. 11*a* and 11*b* at 150 magnification and Figs. 12*a* and 12*b* at 570 magnification.

TABLE V **Change in notched bar impact values of 18 : 4 : 1 high speed steel and 1%C, 1·4% Cr ball-bearing steel at room temperature 21°C before and after remelting.**

Sample			Impact values at room temperature (21°C) (food-pounds)
H.F.	520	(*a*) High frequency melt	(i) 3·61 (ii) 3·8 (iii) 3·9
		(*b*) E.S.R.	(i) 4·33 (ii) 5·2 (iii) 3·9
H.F.	505	(*a*) High frequency melt	(i) 6·0
		(*b*) E.S.R.	(i) 9·0



13 *Curves showing the impact test values of 1%C, 1·4% Cr steel before and after electro-slag remelting at various temperatures.*

Electro-slag refined steels possess better mechanical properties compared with the conventionally manufactured steels, particularly in relation to toughness and ductility. Table V shows the results of Charpy Impact tests conducted at room temperature (21°C) on 18 : 4 : 1 high speed and 1%C, 1·4% Cr steels. Curves indicating the impact test values at different temperatures ranging from 30°C to −40°C of 1% C, 1·4% Cr ball-bearing steel are shown in Fig. 13.

Discussions

It will be observed from Table I that during electro-slag refining with 70 : 30 (CaF_2, Al_2O_3) slag, there is a heavy reduction in the sulphur contents of the steels. These results are supported by the previous workers Paton et al.[3, 4] Moreover, there is no other appreciable change, during the process of remelting, in other elements like C, P, Si, Mn, Cr, W, V, as reported by Zabaluev.[5] These variations can normally be adjusted by keeping suitable allowances in the billet composition and adjusting the slag constituents, whilst other authors[5],[6] have suggested ways and means to avoid the loss of easily oxidised elements in steel such as Al, Ti, etc. Phosphorus is another harmful impurity in steels; the work of Medovar et al[7] confirms that 25-30% of the phosphorus can be removed during electro-slag remelting without affecting other easily oxidisable elements present in the steel by the addition of barium oxide in the working flux with slight adjustments in its other constituents.

Gas analysis by vacuum fusion technique (Table IV) in case of 1% C, 1·4% Cr steel showed a reduction of 20% in oxygen and 13·5% in hydrogen contents therein. The reduction in oxygen is directly related to the content of oxide inclusions in steel and so is the sulphur content with sulphide inclusions. As can be seen from the microphotographs in Figs. 7, 8, 9 and 10 for inclusion count there is a remarkable improvement in the number, shape and size of inclusions after electro-slag remelting. Inclusion study of ball-bearing steel based on J. K. Chart also reveals the absence of sulphide and silicate inclusions after electro-slag remelting. In these experiments a flux consisting of 70 : 30 CaF_2-Al_2O_3 has been used and sulphur reduction varied from 33 to 75% (Table I) and inclusion counts also showed a decrease in the non-metallic inclusion contents and their percentage reduction varied from 25 to 64% (Table II). These findings are in conformity with those of various workers (Table VI) who have used different types of slags.

Findings of various workers using different types of slags.

Ref. No.	Workers	Slag used	Remarks
1.	Latash., Yu. V. et al	(Note taken from B.S.C.R.A. Nov. '61)	Degree of the removal of sulphide is governed by the desulphurising capacity of the flux.
4.	Plechum, G. V.	(Abstract Journal-Metallurgy B 1/2) Expt. on 3-phase electro-slag furnace.	Sulphur content decreases by a factor 1·5–2, the amount of non-metallic inclusions decreases from 0·0135 to 0·0041%.
6.	Medovar, et al	(B.S.C.R.A. Jan. '62)	Use was made of 18/9 stainless steel containing Mn and Ti for investigating the factor affecting easily oxidisable element in steel during E.S.R.
8.	Tregubenko Speranskii and Lerbenzon	(1) ANF-6, CaF_2-Al_2O_3 system) 65% CaF_2, 30–35%Al_2O_3, 3–6% CaO and $\ngtr$1% ($MgO+SiO_2+FeO$)	1. (*a*) Inclusion in ball-bearing steels reduced by 50–60%. (*b*) In 1 Kh 18N9T titanium stabilised stainless steel the titanium loss ranges from 60–90% at top and bottom of the electro-slag cast ingot.
		(2) Pure CaF_2 (slag bath shielded with argon gas)	2. Greatly reduces the melting losses of Ti and uniform distribution of Ti was obtained. Only effective with ingots 250 mm diameter.
		(3) ANF –1(p) (prepared in laboratory)	3. Same results as from pure CaF_2, only needs more trial with 1 Kh 18 N 9T steels.
9.	Robinson, N. and Grainger, J. A.	CaF_2 Al_2O_3 (70 : 30)	1. S reduces from 2 to 8 times (26–88% depending on steel composition) 2. Loss of Ti in Ti bearing stainless steel 80%. 3. Reduces number and size of the inclusions.
10.	Garevskikh, et al	ANF-6 Flux (70 : 30) flux containing (14·8–32·9% Al_2O_3)	In ball-bearing steel, degree of desulphurisation is 25–30% and the final S is proportional to the initial content. Cleanliness of steel (with respect to sulphide and globular inclusion) improved with an increase in the alumina content.
11.	Medovar, et al	B.S.C.R.A. No. 62 flux should contain no oxide which can be easily reduced by the elements (like Ti and Al present in steel). Other precautions: well pickled surface, no scales, inert atmosphere, and closer arc to avoid oxidation by heating of the rod.	
12.	Klyuev, et al	1. Effect of shielding the slag bath and the electrode tip to lessen oxide inclusions. 2. Use of used slags for remaining oxide inclusions.	1(*a*) O_2 reduced from 0·005–0·300% covered mould. (*b*) O_2 reduced from 0·005–0·002% bath shielded with N_2 2. Caused globular inclusion to develop.
13.	Pridantsev, et al	ANF-6 (30–40 Al_2O_3, 60–70 CaF_2) and ANF-6 with TiO_2	Produced unsatisfactory macro-structure in Fe-Cr-Ni base alloy KhN-35-VTYU susceptibility to non-axial segregation and spot segregations in ingots.
		ANF-291(39–43% Al_2O_3, 16–20% CaF_2 22–36% CaO, 14–20% MgO) and ANF–6+15% MgO	Ingots produced with these slags did not show any spot or non-axial segregation.

The electro-slag remelted ingot structure of a medium carbon steel, as shown in Fig. 5, is free from porosity, axial segregation, piping and columnar structure. The high speed steel ingot section (Fig. 6) shows the absence of carbide heterogenity in eletro-slag remelted ingot. These observations are in conformity with the results of other workers. The importance of a specific ingot design regarding a definite ingot cross section/length ratio is not so great since following the mode of solidification in electro-slag remelting, the ingot does not exhibit any shrinkage cracks or massive carbide segregations.

The superior macrostructure of the steel ingots and lowered non-metallic inclusions lead to far improved isotropy in mechanical properties, better forgeability, mechanical workability and tool life. The impact properties at room temperature (Table V) shows improved toughness of the electro-slag remelted steel.

Conclusion

Electro-slag remelting produces ingots free from axial porosity and segregation by virtue of the mode of solidification. The process of electro-slag remelting definitely improves the quality of steel with respect to reduction of sulphur to very low levels, reduction of non-metallic inclusions, production of much superior ingot surface finish and better mechanical and impact properties.

Acknowledgement

The authors wish to thank Shri D. P. Chakravarty for assistance in the experimental work and preparation of metallographic specimens and also wish to thank Dr H. P. Bhattacharya and his colleagues for chemical analyses and Shri N. G. Banerjee for gas analysis.

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Recovery of Zinc and Lead from the Slime Obtained from Electrolytic Zinc Plant

Narinder Singh
Mgr. Inz. Jan Sosin

Keeping in view the projected primary zinc smelting plants in India expected to yield a large amount of slime (a by-product) containing a economically recoverable percentage of zinc and lead, this investigation was taken up for determining the optimum conditions for the economic recovery of metals from the slime. The slime sample obtained from the electrolytic zinc plant in Szopienice, Poland was investigated during one of the authors' stays in Poland under UNESCO Polish Government Fellowship. The experiments were performed in an electric furnace at different temperatures with the varying additions of coke dust and lime. It was concluded that the addition of 14% lime to the slime with 50% coke additions gives the maximum metal recovery. The authors are of the opinion that the experiments, if extended onto a pilot plant scale, using a small rotary furnace, will give more useful results.

THE entire requirements of zinc metal in India are at present met by imports. However, the envisaged production of zinc from indigenous and imported zinc concentrate by the end of the Third Plan period (1965-66) is about 27 000 tonnes/year, which will be produced by zinc smelters being set up at Udaipur (Rajasthan) and at Alwaye in Kerala State. Another electrolytic zinc plant is also expected to be set up in the vicinity of Visakhapatnam with Polish collaboration. The electrolytic process of producing zinc up to 27 000 tonnes is expected to yield about 4 000 tonnes of electrolytic slime containing about 20% Zn and 5% Pb, which can be recovered by suitable treatment. With this and in view, the problem of recovery of zinc and lead from the slime from an electrolytic zinc plant in Poland was taken up by the authors.

1 *Set-up for melting point determination by Baunte Baume method.*

Theory

The recovery of zinc as zinc oxide is based on the reduction of the latter with carbon, the evolved zinc vapours being burned to oxide. Depending on the type of furnace used three methods may be considered :

(i) Grate method
(ii) Slag fuming method
(iii) The Waelz process

The Waelz process is widely used in Germany, Poland and the Soviet Union for recovery of zinc from ores and other by-products with a low content of volatile metal by heating in a revolving kiln up to the temperature required for volatilizing the metal to be recovered. The vapours are carried away with the kiln gases and recovered in the form of oxides very rich in metal content. This process can treat ores, tailings, middlings, slimes, ashes, slags and various types of residues.

In Poland, the rotary furnaces used for this purpose in the Zaktady Gorniczo-Hutnicze BOLESLAW zinc

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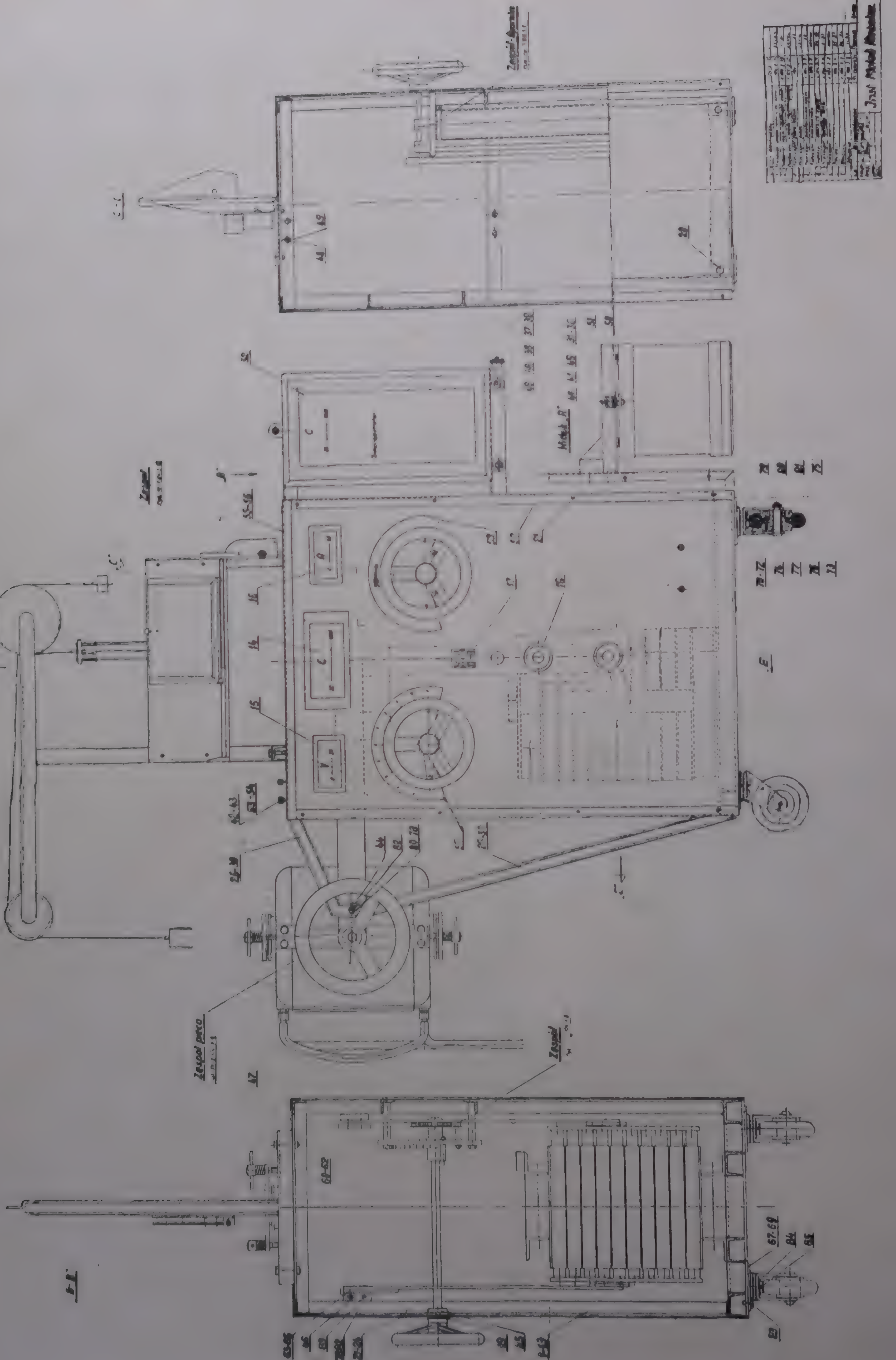
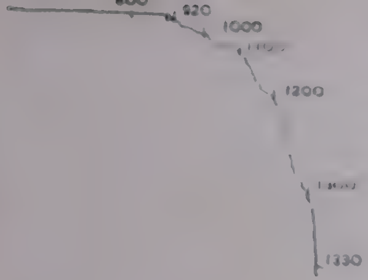
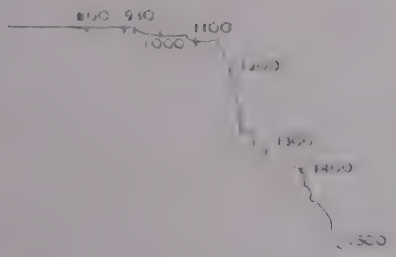


2 Sketch showing Baunte Baume apparatus.



Charge	100% slime 390 gm
$\triangle T$	50°C/5 min constant
Beginning of melting	920°C
End of melting	1 330°C
Metal vapours escaped at	980°C
Time of melting	41 min

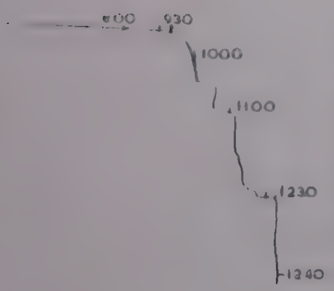
3a



Charge	100% slime 390 gm
$\triangle T$	50°C/5 min constant
Beginning of melting	930°C
End of melting	1 500°C
Metal vapours escaped at	960 C
Time of melting	57 min

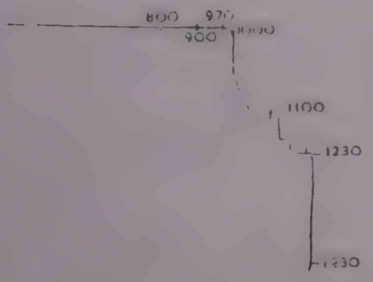
(From temp. 0–1 500 C only 88% of sample was melted)

3b



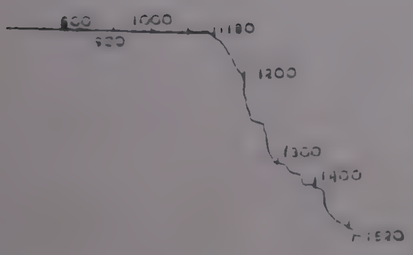
Charge	100% slime 390 gm
$\triangle T$	50°C/ min constant
Beginning of melting	930°C
End of melting	1 240°C
Metal vapours escaped at	920°C
Time of melting	31 min

3c



Charge	100% slime 390 gm
$\triangle T$	50°C min constant
Beginning of melting	970°C
End of melting	1 230°C
Metal vapours escaped at	920°C
Time of melting	24 min

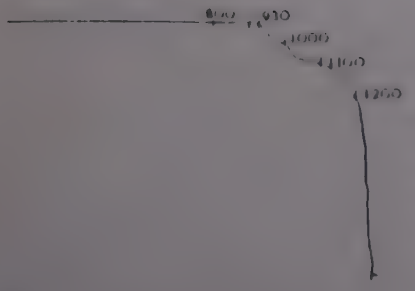
3d



Charge	100% slime+30% coke 390 gm
$\triangle T$	50°C/5 min constant
Beginning of melting	1 180°C
End of melting	1 520°C
Metal vapours escaped at	1 090°C
Time of melting	40 min

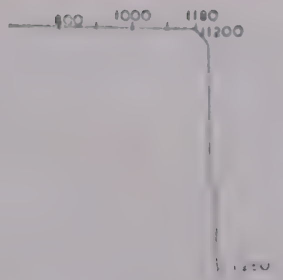
(From 0 to 1 500°C metal melted 78% only)

3e



Charge	100% slime + 10% coke 930 gm
$\triangle T$	50 C 5 min constant
Beginning of melting	930 C
End of melting	1 260°C
Metal vapours escaped at	970°C
Time of melting	33 min

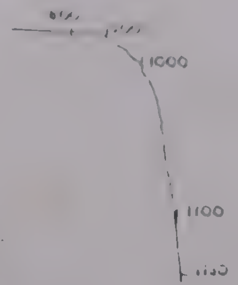
3f



Charge	100% slime+50% coke 390 gm
$\triangle T$	50°C/5 min constant
Beginning of melting	1 180°C
End of melting	1 250°C
Metal vapours escaped at	1 120°C
Time of melting	7 min

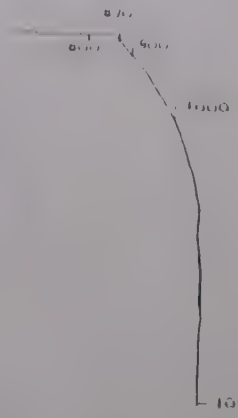
(As the sample became powder, perhaps melting did not take place)

3g



Charge	100% slime+5% CaO 390 gm
$\triangle T$	50°C/5 min constant
Beginning of melting	800°C
End of melting	1 130°C
Metal vapours escaped at	890°C
Time of melting	31 min

3h



Charge	100% slime 390 gm
$\triangle T$	50°C/5 min constant
Beginning of melting	870°C
End of melting	1 090°C
Metal vapours escaped at	860°C
Time of melting	20 min

3i

plant are 40 metres long and of inner diameter of 3 metres and outer diameter of 3·5 metres with an inclination of 3–4°. Each furnace yields 0·5–0·6 tonne/m³ per 24 hr. The speed of rotation of the furnace is 0·5–0·75 rpm.

The amount of zinc in the charge ranges from 7 to 12% and in the residue 0·8–2% is left. Zinc losses amount to 15–20% and the metal recovery is about 70–75%. The furnaces use coal dust as fuel. The furnace at the new plant at Miasteczko will be 95 metres long with an internal diameter of 4 metres and an external diameter 4·5 metres.

Chemical reactions

The raw materials containing zinc in the form of zinc oxide, zinc ferrite, zinc silicate or zinc sulphide are mixed with any carbon containing fuel. The following reactions take place in the furnace:

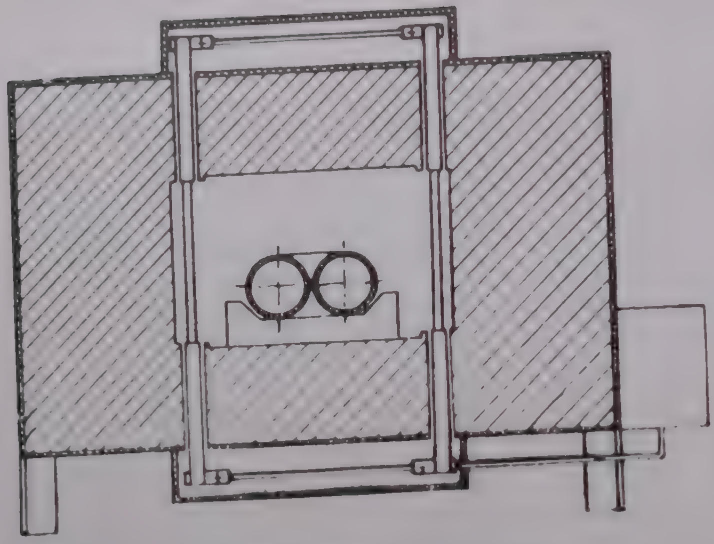
$$ZnO + C = Zn\ (vapour) + CO - 53\,844\ kcal \quad (1)$$

$$Zn\ (vapour) + CO + O_2 = ZnO + CO_2 + 151\,040\ kcal \quad (2)$$

The first reaction takes place within the charge and is endothermic, while the second reaction takes place on the surface of the charge and is exothermic. Adding both the equations:

$$C + O_2 = CO_2 + 97\,200\ kcal \quad \dots \quad (3)$$

It is clear from the above that once reaction is started, no fresh supply of heat is required, though there are some heat losses. If the zinc is present in the form of silicate and ferrite, the same reactions take place, but if the zinc is in the form of sulphide, it is decomposed by CaO or FeO as follows:



4a Sketch of electrically heated U tube furnace.

$$ZnS + CaO + C = Zn\ (vapour) + CaS + CO - 51\,040\ kcal \quad \ldots \tag{4}$$

$$Zn\ (vapour) + CO + O_2 = ZnO + CO_2 + 151\,040\ kcal \tag{5}$$

$$ZnS + FeO + C = Zn\ (vapour) + FeS + CO - 55\,540\ kcal \quad \ldots \tag{6}$$

$$Zn\ (vapour) + CO + O_2 = ZnO + CO_2 + 151\,040\ kcal \tag{7}$$

$$CaSO_4 + 4C = CaS + 4CO_2 \quad \ldots \tag{8}$$

$$CaS + SiO_2 + ZnS = (CaS.SiO_2) + ZnS.$$

The decomposition of zinc sulphide needs a higher temperature than the reduction of zinc oxide. In addition the reactions (5) and (7) are exothermic and liberate a large amount of heat.

Objective

On the basis of the Waelz process, the problem was taken up by the authors to determine the optimum conditions for recovery of zinc and lead from the slime obtained from the electrolytic process of zinc making.

The optimum amount of reducing agent (coke) and the percentage of lime as a decomposing agent to decompose Zn and Pb sulphides present in the slime and optimum temperatures of reactions were determined. In the absence of a small experimental rotary furnace, the experiments were performed in a stationary electrical furnace. An air blast simulated the conditions of a rotary furnace. However, continuous tumbling of the charge could not be created in the stationary furnace.

	%		%		%
Zn	19·94	Pb	4·82	Cd	0·27
CaO	6·37	MgO	1·57	SiO_2	2·30
S	10·77	Al_2O_3	0·92	Fe	35·83
H_2O	33·03 in wet slime				

TABLE II Chemical analysis of coke ash %

Ash	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	S	H_2O
11·90	6·43	3·60	38·93	19·66	21·95	0·90	2·70

TABLE III Seive analysis of coke

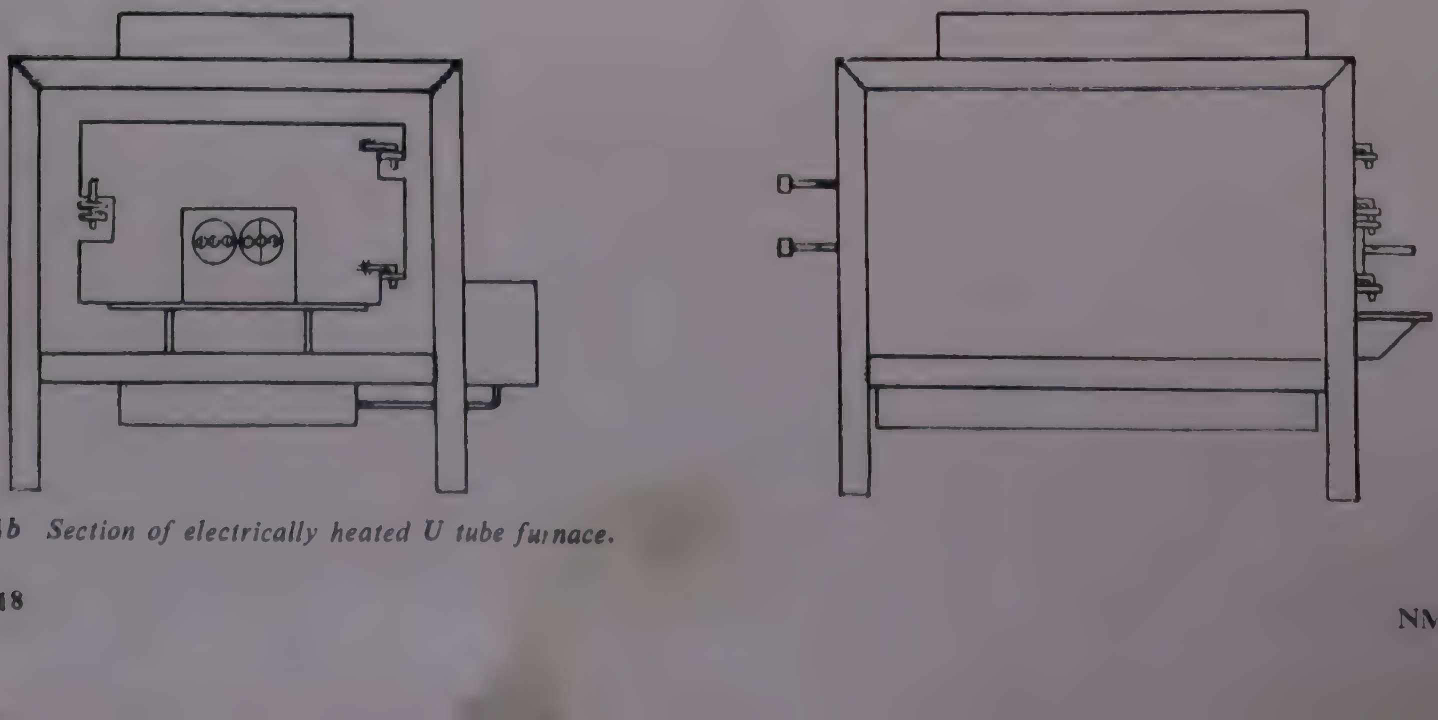
Sized sieve, mm		% passing
0·63	...	64
0·315	...	14·9
0·25	...	3·0
0·16	...	6·3
below 0·16	...	11·8

Experimental

A representative sample of the electrolytic slime from the zinc works 'Zaktady Cynkowe SZOPIENICE' in Poland was obtained for the experiments. From the main sample, two representative samples were taken: one part was chemically analysed and the other was well dried in a drying furnace and divided into three samples for determining the melting point by Baunte Baume method. The apparatus of Baunte Baume type designed and fabricated at the Instytut Metali Niezelaznych, Gliwice is shown in Figs 1 and 2.

The melting point of the mixture of slime with coke and with lime was also determined from time to time as the experiment progressed. The results are given in Figs. 3*a* to 3*g*. Sieve analysis of granulated coke dust was carried out; the ash from the coke was also chemically analysed (Tables II and III respectively).

The experiments for the recovery of zinc and lead were performed with the addition of 40 and 50% coke dust. About 200 grams of wet slime were taken from the main sample and 40% of coke dust was added to it (the addition of coke was on the basis of 100% of dry slime). The charge was well mixed and introduced into a pre-weighed steel boat which was then placed into the U tube of an electrically heated furnace (Figs. 4*a* and 4*b*), which was already heated to pre-determined



4b Section of electrically heated U tube furnace.

water cooled screws and air at a pressure of 420 mm of water column (12 litres per minute or one volume of U tube per minute) was passed through the U tube. The air pressure was controlled by the manometer. The evolution of water vapours and gases took place from the open outlet of the U tube. After some moments the Zn and Pb vapours were also observed to be escaping from the tube. After two hours the furnace was put off, the boat with the charge was taken out, cooled and weighed. The product after reduction was analysed.

After determining the optimum quantity of coke, tests were performed with the addition of 5%, 10% and 15% of lime at the suitable temperature. The results are contained in Table IV.

Results and discussions

It can be seen from the Figs. 3*a* and 3*b* giving the melting curves determined by Baunte Baume method that pure slime without any external additions starts melting at 930°C in the 1st sample and at 970°C in the 2nd and the melting ended at 1 240°C and 1 230°C respectively. The temperature of distillation of metal was 920°C in both samples. As such, it can be deduced that on an average the slime started melting at about 950°C and ended melting at about 1 235°C. Accordingly, it was decided to perform the experiments at temperatures between 1 050°C and 1 100°C

Figures 3*c*, 3*d* and 3*e* give the graphs of melting point determination by Baunte Baume method with the addition of 30%, 40% and 50% of coke respectively.

From Figs. 3*f* and 3g showing the curves of the melting point determination with the additions of 5 and 15% of CaO to slime (on dry weight basis), it can be seen that the charges begin to melt at 800°C and 870°C and stop melting at 1 130°C and 1 090°C respectively, while the temperatures of distillation of metal are 890°C and 860°C respectively It shows that the melting point is unusually lowered by the addition of CaO to the charge. This may be explained by the following reactions :

$$Fe(OH)_3 = Fe_2O_3 + H_2O$$

$$Fe_2O_3 + CaO = Fe_2O_3.CaO$$

Iron in the slime is present in the form of $Fe(OH)_3$ which decomposes to Fe_2O_3 and water. Fe_2O_3 with CaO forms a compound $Fe_2O_3.CaO$. As the melting point of this compound is below 1 200°C, its presence in the Baunte Baume method of melting point determination where coke is not present, reduces the melting point of charge. On the contrary, in the furnace where the charge contained carbon also, this phenomenon is not observed, because in the furnace, the reduction takes place at 500°C and the compound $Fe_2O_3.CaO$ is not formed. From Table I, it can be seen that the slime from the SZOPIENICE Zinc Plant contains about 20% Zn and about 5% Pb. Table IV gives the results of the tests performed for recovery of Zn and Pb with varying additions of coke and lime.

The experiments on laboratory scale show that the optimum temperature for the recovery of zinc from slime by the method described above is 1 050°C. This is proved by results from experiments 1, 2 and 3. In the experiment No. 1 carried out with a minimum temperature of 1 050°C, the recovery was 70·05%, at the temperature 1 075°C (experiment No.4) the recovery was 48·06% and at the temperature 1 100°C (experiment No. 3) the recovery was only 26·55%. Such influence of temperature can be seen by comparing experiments No. 5 and 7.

TABLE IV Results of experiments

No.	Composition of charge		Temp. °C	CHARGE														PRODUCT												
	Coke %	CaO %		Wt gr	Slime dry gr	CaO gr	Coke gr	Ash from coke gr	Zn			Pb			C in Coke			Wt after red gr	Loss in wt gr	Zn				Pb				C		
									% An	gr	% charge	% An	gr	% charge	% An	gr	% charge			% An	gr	% charge	% rec	% An	gr	% charge	% rec	% An	gr	% charge
1	40	-	1050	200	103.1	-	41.27	4.91	19.94	20.57	100	4.82	4.97	100	88.10	36.30	100	88.4	112.6	6.97	6.16	29.95	70.05	1.1	0.97	19.5	80.50			
2	40	-	1050	200	103,1	-	41.27	4.91	"	20.57	"	"	4.97	"	"	36.30	"	91.3	108.7	6.18	5.64	27.42	72.58	1.23	1.12	22.53	77.47			
3	50	-	1100	266.0	115.3	-	57.63	6.86	"	22.98	"	"	5.56	"	"	50.77	"	116.5	149.5	14.49	16.88	73.45	26.55	1.02	1.19	21.40	78.60	14.02	16.5	32.16
4	50	-	1075	216.5	139.3	-	69.2	8.23	"	27.78	"	"	6.71	"	"	60.96	"	114.5	102.1	12.6	14.43	51.94	48.06	1.70	1.95	29.10	70.90	22.94	26.3	43.14
5	50	5	1075	268.7	128.8	6.4	64.4	7.66	"	25.69	"	"	6.21	"	"	57.64	"	130.5	138.2	15.48	20.21	78.67	21.33	1.35	1.76	28.34	71.66	11.14	14.5	25.55
6	50	14.2	1075	273.5	130.0	18.5	65.0	7.73	"	25.92	"	"	6.27	"	"	57.26	"	146.4	127.1	8.73	12.78	49.34	50.66	1.48	2.17	34.60	65.40	12.10	17.7	30.91
7	50	5	1050	275.0	131.6	6.5	65.8	7.83	"	26.25	"	"	6.35	"	"	57.97	"	150.0	125.0	10.49	15.73	59.92	40.08	3.14	4.71	74.17	25.83	21.65	32.28	55.70
8	50	10	1050	278.0	130.0	13.0	65.0	7.73	"	25.92	"	"	6.27	"	"	57.26	"	151.0	127.0	8.32	12.56	48.46	51.54	2.50	3.77	60.13	39.87	16.39	26.75	46.22
9	50	14.2	1050	263.5	121.5	17.18	60.9	7.24	"	24.20	"	"	5.87	"	"	53.65	"	122.0	141.5	5.76	7.06	29.02	70.98	2.41	2.94	50.08	49.92	15.44	16.40	30.57

These experiments were performed with an addition of 5% of lime. In experiment No. 5, the recovery of Zn was 40·08%. Similar comparison can be made between experiments No. 6 and 9 which were performed with the addition of 14% of lime at 1 075°C and 1 050°C respectively. It was seen that the recovery of zinc was 50.66% and 70·98% respectively. From the results, it is obvious that the addition of lime in the charge has not given the expected results i.e. the high recovery of zinc with increased basicity of the charge.

However, it should be noted that with increased lime content, recovery of zinc was better, particularly by increasing the lime content from 10 to 14%. The rate of burning of coke in the experiments performed at higher temperature (Nos. 3, 4, 5 and 6) is higher than in those performed at 1 050°C. But this influence is not so clear. The percentage of recovery of lead without addition of lime is higher than in experiments with the addition of CaO ; at the range of 1 050°C to 1 100°C, the great difference in percentage of recovery of lead is not observed.

The influence of the addition of lime at 1 075°C is insignificant but by comparing the results of experiments Nos. 5 and 6, it can be stated that with an addition of 14% of lime, the percentage of recovery of lead is less than that with the addition of 5% of lime. In experiments carried out with the addition of lime at 1 050°C (experiments 7, 8 and 9), the percentage of lead recovery is very low and increases with increased lime content. This phenomenon of better recovery with increased lime content is not clear. Theoretically there should be a decrease in the recovery of lead with increased CaO content.

To summarise the results, the addition of lime above 14% is useful for recovery of zinc and lead from the slime. This is supported by the experiments earlier carried out by Instytut Metali Niezelaznych (Institute of Non-ferrous Metals), Gliwice, Poland, on industrial scale by using a few thousand tonnes of slime obtained from Polish zinc plants when the recovery of zinc and lead is achieved to the extent of 93% and 95% respectively.

Scope of further work

For creating conditions simillar to those in an industrial plant, the experiments may be performed on a semi-

furnace. The rotary furnace may be designed to have about 5 metres length, outer diamcter of about 1 metre, internal diameter of about 500 mm with lining of 250 mm thickness and having an inclination of 4 to 5 degrees and a speed of 1 to 4 rpm. A mechanism for varying the inclination of the furnace to about 2% would provide additional focilities for trial.

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Studies on the Preparation of Cryolite by Fluoboric Acid Process

Gurdial Singh
B. C. Kar

Calcium fluoride, boric acid and sulphuric acid react in an aqueous medium with the formation of fluoboric acid. The reaction goes practically to completion when pure materials are used. Fluoboric acid thus formed can be utilized for the formation of cryolite and other fluorides.

A cyclic process for the production of cryolite from metallurgical grade fluorspar, sulphuric acid and boric acid has been studied in this paper. The intermediate product, fluoboric acid, which is formed, is reacted with hydrated alumina and sodium carbonate to form cryolite while boric acid is regenerated. The spent liquor containing boric acid is cycled a number of times to get more fluoboric acid and thence cryolite.

CRYOLITE is the mineral form of sodium fluoaluminate, Na_3AlF_6 or $3NaFAlF_3$. Natural cryolite,[1] when pure, is colourless to snow-white, transparent to translucent and has a vitreous to greasy lustre. It resembles ice when immersed in water. Cryolite is one of the essential minerals in the present industrial age. It is required chiefly by ceramic and aluminium industries. At present all the cryolite required for Indian industries is being imported from Denmark and Greenland. Production of one tonne of aluminium requires 0·1 tonne[2] of cryolite approximately. The country's aluminium industry alone will therefore need 7 500 tons of cryolite annually. With the expansion of the aluminium industry, the demand for cryolite will almost be doubled at the end of the Third Five Year Plan. The only known commercial deposit of cryolite is situated at Ivigtut, Greenland. The mine is owned by the Danish State. The first specimens of cryolite were exported from Greenland in 1808 but the mineral did not attain commercial importance until the mid-century. While there is no cryolite deposit in India, fluorspar,[3] the raw material for the production of cryolite, occurs in Dungarpur district, Rajasthan, Drug district, Madhya Pradesh and Baroda district, Bombay. The deposits are low-grade containing a high percentage of silica. It has been estimated that about 2·5 million tons of fluorite ore containing 20–30% calcium fluoride exists in Dungargur district, Rajasthan and about 46 000 tons and 104 000 tons of ore containing 26–30% calcium fluoride occur in Nandgaon and Kairagarh respectively in Madhya Pradesh. These fluorspar deposits, being of low grade, need to be beneficiated before processing for the production of cryolite. Extensive work on beneficiation of fluorspar on laboratory scale and pilot plant scale has already been carried out in the National Metallurgical Laboratory.

Methods of production

Several methods have been developed for recovering fluorine from different grades of fluorspar.[4] The simplest method for the production of synthetic cryolite from fluorspar involves the neutralization of hydrofluoric acid with soda ash and hydrated alumina in the proportions occurring in cryolite. The reaction may be represented as

$$3Na_2CO_3+Al_2O_3.3H_2O+12HF$$
$$=2Na_3AlF_6+3CO_2+9H_2O$$

By varying the ratio of soda ash and hydrated alumina, it is possible to make mixtures of cryolite $3NaF.\ AlF_3$ and chiolite $5NaF.3AlF_3$ or mixtures of cryolite with either excess sodium fluoride or aluminium fluoride.

Hydrofluoric acid is first made by treating acid-grade fluorspar and sulphuric acid in suitable iron kilns. Acid grade fluorspar generally contains calcium fluoride not less than 97% and silica not more than 0·5%. The mixture of ground fluorspar and sulphuric acid is continuously stirred while passing through heated iron kilns and the hydrofluoric acid which is liberated is absorbed in water in suitable cooling and absorbing towers.

The corrosive nature of the intermediate product, hydro-fluoric acid, is a drawback of this process. Hydrofluoric acid in gaseous as well as liquid form is very difficult to handle and is highly corrosive. At the same time, the fluorspar from which hydrofluoric acid is obtained need be of very high grade and practically free from silica.

Another process,[5] which has recently been developed for the preparation of cryolite, involves the treatment of -200 mesh crude fluorspar containing CaF_2 40–50%, silica 30–40% with sulphuric acid at a temperature of about 300°C in suitable retorts. Fluosilicic acid is formed and the gas containing fluosilicic acid and hydrofluoric acid is bubbled through condensers when a solution of hydrofluosilicic acid is obtained. The solution of fluosilicic acid is then neutralized with gaseous ammonia and excess ammonia is added to decompose ammonium silicofluoride when sillica is precipitated in a granular form. To the ammonium fluoride solution is then added an equivalent amount of sodium aluminate to form cryolite. Ammonia gas liberated during precipitation, is recycled.

An advantage of this process is that low grade fluorspar containing a high percentage of silica can be used as such. But complete removal of silica from the final liquor is very difficult and the product is contaminated with silica which makes it sometimes unsuitable for the aluminium reduction cell. This method is suitable for the recovery of fluorine from effluent gases from the superphosphate fertilizer industry.[6] Fluosilicic acid is obtained as a by-product which can be processed into cryolite by the above process.

The third process which has been investigated at the National Metallurgical Laboratory consists in decomposing metallurgical grade fluorspar in an aqueous

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medium with sulphuric acid in the presence of boric acid when fluoboric acid is formed. The reaction can be represented by the equation

$$2CaF_2+2H_2SO_4+H_3BO_3+H_2O = HBF_4+2CaSO_4.2H_2O \quad \ldots \quad (1)$$

A notable feature of the process is that silica is not attacked by fluoboric acid and is removed with the calcium sulphate. Fluoboric acid formed by the above reaction is neutralized with hydrated alumina and sodium carbonate to form cryolite. Boric acid is regenerated. The reaction can be represented by the equation

$$3HBF_4+Al_2O_3.3H_2O+3Na_2CO_3 = 2Na_3AlF_6+3H_3BO_3+3CO_2 \quad \ldots \quad (2)$$

Cryolite is filtered and the filtrate can be recycled for leaching fresh fluorspar.

Equation (1) represents a reaction that goes to completion with pure calcium fluoride and sulphuric acid with excess of boric acid. Reversible reaction is retarded as the fluoborate ion is poorly dissociated. Calcium sulphate is appreciably soluble in fluoboric acid solution and its solubility increases with increase in temperature. To produce pure cryolite. it is necessary to produce fluoboric acid practically free from calcium ion.

An excess of sulphuric acid can furnish sulphate ions to suppress the solubility of calcium ions ; but free sulphuric acid is undesirable because this cyclic process, for the preparation of cryolite, cannot function properly in the presence of free sulphuric acid. Sulphuric acid interferes with the precipitation of cryolite as represented by the equation

$$3H_3BO_3+2AlF_3.3NaF+6H_2SO_4=3HBF_4 +3NA_2SO_4+Al_2(SO_4)_3+9H_2O \quad \ldots \quad (3)$$

Consequently, it is necessary to employ sodium sulphate as a constant component to supply sulphate ions. Sodium sulphate is suitable because sodium ions are common in the process liquors. Concentrations of sodium sulphate have been used in the process within the range of 50 to 100 gm/l. These concentrations suppress the solubility of calcium but never eliminate it completely. As a result the cryolite produced by the process is never completely free from calcium and sulphate although these are always controlled within specified limits.

In all our experiments, using the weight ratio of alumina to soda of 1 : 1 for precipitation of cryolite from fluoboric acid solutions, it was found that AlF_3 content in the cryolite was always higher than the formula represented by $AlF_3.NaF$. So it is assumed that the cryolite obtained was a mixture of cryolite plus aluminium fluoride.

Experimental procedure

Metallurgical grade fluorspar obtained by the beneficiation of low-grade fluorspar was used for our experiments. The concentrates had the following compositions :

CaF_2–84·37%, $CaCO_3$–9·2%, SiO_2–3·8%, Fe_2O_3 –0·34%, Al_2O_3–1·28%, MgO–0·36%, S–trace, moisture –0·04% and loss on ignition –6·36%.

Beneficiated fluorspar, as received, contained some coarse particles. It was passed through 150 mesh sieve and minus fraction was taken for experiments. Preliminary leaching experiments were carried out with varying amounts of sulphuric acid, boric acid and sodium sulphate at different temperatures, for different intervals of time and with different amounts of fluorspar. The amount of fluorspar leached with one litre of leach liquor was kept at 200 gm. Amounts more than 200 gm per litre were difficult to handle because the resultant calcium sulphate

heating of the slurry. Boric acid was always used in excess of the quantity theoretically required. Boric acid concentration was kept between 110 gm and 120 gm per litre. The theoretical amount of sulphuric acid and down to 95% of the theoretical amount was used, but it was always found that the resultant digest liquor contained some residual sulphuric acid. Sodium sulphate was kept as a constant component of the process and 20 to 70 gm/litre were used. It was found that 50 gm/litre sodium sulphate was quite sufficient to keep the calcium content at a minimum. Time and temperature are quite complementary to each other. At temperatures lower than the finally selected 95°C, leaching efficiency was as high as 85% but at a considerably longer interval of time. At 95°C, leaching for two hours with continuous stirring gives fluorine extraction from 95 to 98 per cent. The speed of stirring the slurry does not have much influence on the extraction of fluorine as the slurry is in continuous motion. The optimum conditions for leaching were as follows :

Five hundred c.c. of the leach liquor were synthesised from water, pure boric acid and pure sodium sulphate and the requisite amount of sulphuric acid was added. It was placed in a one litre beaker fitted with an electric stirrer. The liquor was heated to 80°C with a burner and fluorspar was gradually added by gently sprinkling small amounts into the agitated liquor over a period of 30 to 40 minutes so that the resultant calcium sulphate is granular. If the fluorspar is added quickly, the slurry gets thickened, which creates difficulty in stirring and filtration. The temperature was raised to 95°C and the stirring continued for two hours keeping the volume constant with hot water. The slurry was then cooled to room temperature and filtered.

After standardising the leaching conditions, experiments for the precipitation of cryolite were carried out with varying amounts of hydrated alumina and sodium carbonate. The residual sulphuric acid was always removed with calcium carbonate before proceeding for precipitation. Calcium carbonate reacts with sulphuric acid to form calcium sulphate which is precipitated and filtered out.

In the precipitation of cryolite when theoretical amounts of hydrated alumina and sodium carbonate were used, the precipitation was not complete and there was a sodium sulphate build-up in the liquor which consequently lowered the leaching efficiency. Experiments were conducted by varying the ratio of hydrated alumina to sodium carbonate and it was found that 1 : 1 ratio by weight gave better results. So equal amounts of hydrated alumina and sodium carbonate were used for precipitation in subsequent experiments.

Digest liquor containing fluoboric acid was heated to 95°C and a calculated amount of hydrated alumina was added while stirring the liquor. After half an hour of the alumina addition the requisite amount of sodium carbonate was slowly added over a period of forty minutes continuously stirring the liquor and keeping the temperature 95°C. Digestion was continued for another half an hour for the reaction to complete. During this period, the volume of liquor was kept constant by adding hot water or wash water. The slurry after cryolite precipitation was not allowed to cool because boric acid might crystallise and get removed along with the cryolite. The final solution at the end of the cryolite precipitation was kept acidic to avoid the coprecipitation of iron along with cryolite. Cryolite was then filtered while still hot in a Buchner funnel with water suction pump. Glass apparatus was used for leaching and precipitation as it is not attacked by fluoboric acid. Cryolite was washed until the wash water was neutral. The cryolite cake was removed and dried at 400°C in a porcelain basin for two to three hours. The temperature while drying was raised slowly because cryolite dissociates into alumina and hydrofluoric acid in the presence of water if heated quickly.

The process is very simple and works at overall efficiencies of more than 95% in the first cycle. A cycle is made up of one leaching of fluorspar, chemical analysis of leach liquor, removal of residual sulphuric acid and finally precipitation of cryolite. To make the best use of boric acid, which is regenerated during precipitation of cryolite, the spent liquor after filtration of cryolite is used again for leaching fluorspar after adding the requisite amount of sulphuric acid.

The flowsheet is shown in Fig. 1.

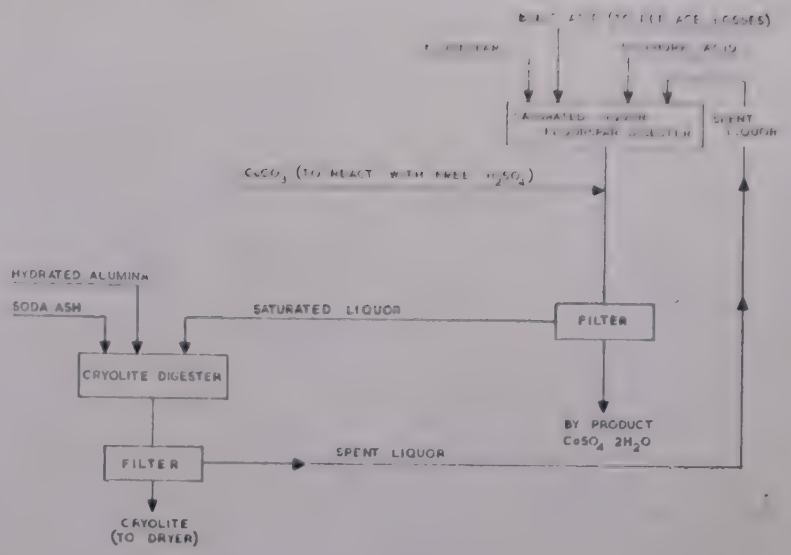
The more cycles one can perform with the same liquor with the requisite efficiency, the better will be the overall economics of the process for commercial exploitation. For cyclic experiments, the precipitation and purity of the spent liquor are the two main considerations. The precipitation is more important because if all the aluminium and sodium are not precipitated there will be build-up of these ions which will upset the efficiency of leaching. Particularly, aluminium fluoride adversely affects the reaction between calcium fluoride, sulphuric acid and boric acid as shown in Table IV. Build-up of sodium sulphate also adversely affects the leaching reaction. In the spent liquor iron is one of the main impurities and the other impurities are lead, manganese, zinc and copper. These impurities generally found in the spent liquor do not affect the leaching efficiency individually but the combined effect of all the impurities does hinder the reaction between fluorspar, sulphuric acid and boric acid to a great extent. Iron can be removed easily by oxidizing it by air and then precipitating it as ferric hydroxide. But it is difficult to remove other impurities. The spent liquor was discarded after a number of cycles when these trace impurities built up to an extent and the leaching efficiency went down. Of course, boric acid can be recovered from these discarded solutions by crystallization as it is not very much soluble in cold water. The spent liquor can be evaporated and cooled to recover boric acid.

Tables I, II and III show the three cyclic experiments to find out how many cycles can be carried out with reasonable recoveries.

In the first cyclic experiment shown in Table I, the leaching went down in the fourth cycle as shown by the large amount of unreacted sulphuric acid. The spent liquor after the fourth cycle was taken and the iron oxidized by passing air and precipitated by the addition of $CaCO_3$. The next four cycles were carried out with the purified solution after replenishing boric acid. Again, in the ninth cycle, the leaching efficiency dropped appreciably and the precipitation was poor. The solution was again purified from iron but leaching did not improve.

In the second cyclic experiment shown in Table II the condition did not improve and remained the same as in cyclic experiment 1.

But in the third experiment shown in Table III, the overall efficiency improved. The starting solution was prepared a little higher in boric acid and more of hydrated alumina and sodium carbonate were used than in the previous cyclic experiments. The leaching efficiency again dropped in the ninth cycle and did not improve even after purification The spent liquors of the three experiments were analysed in the ninth cycle for copper, zinc and manganese spectroscopically and all these were present in the liquors. Although there was sufficient boric acid in the solution, the reaction between fluorspar, sulphuric acid and boric acid did not take place. Boric acid consumption per 100 gm of cryolite produced decreased to 1·93 gm of boric acid in the third cyclic experiment. Overall fluorine recovery increased to 73·5%



1 *Fluoboric acid cryolite process flowsheet.*

TABLE I Cyclic process for the preparation of synthetic cryolite by fluoboric acid method

Cyclic experiment 1

Solution volume	... 500 c.c.
Sodium sulphate	... 25 gm
Temperature of leaching	... 95°C
Time	... 2 hours

No of Cycle	Fluorspar (gm)	Sulphuric acid	Boric acid (gm)	Residual H_3SO_4 (gm)	Sodium carbonate (gm)	Hydrated alumina (gm)	Cryolite obtained (gm)
1	100	Theoretical	55	3·42	34	34	60
2	,,	,,	—	14·37	37·8	37·8	66
3	,,	,,	—	28·40	32·5	32·5	48
4	,,	,,	—	46·00	30·5	30·5	45
Purified							
5	,,	,,	8	26·45	22·5	22·5	45
6	,,	,,	—	30·20	30·0	0·0	48
7	,,	,,	—	40·29	26·0	26·0	46
8	,,	,,	—	37·4	28·0	28·0	47
9	,,	,,	—	47·0	30·0	30·0	20

Total cryolite obtained up to 8th cycle	405 gm
Boric acid in spent liquor	48 gm
Loss of boric acid	15 gm
Boric acid loss/100 gm of cryolite	3·7 gm
Total fluorine in 800 gm of fluorspar	329 gm
Up to 8 cycles fluorine recovered	210·6 gm
Overall recovery	64·01%

TABLE II Cyclic process for the preparation of synthetic cryolite by fluoboric acid method.

Cyclic experiment 2

Solution volume	...	500 c.c.
Sodium sulphate	...	25 gm
Temperature of leaching	...	95°C
Time	...	2 hours

No. of cycle	Fluorspar (gm)	Sulphuric acid	Boric acid (gm)	Residual H_2SO_4 (gm)	Sodium carbonate (gm)	Hydrated alumina (gm)	Cryolite obtained in (gm)
1	100	Theoretical	55	1·9	33	33	64
2	,,	,,	—	2·33	33	33	60
3	,,	,,	—	11·10	34	34	58
4	,,	,,	—	19·30	34	34	53
5	,,	,,	—	33·80	34	34	33
6	,,	,,	20	19·85	28	28	28
Purified							
7	,,	,,	—	6·40	34	34	63
8	,,	,,	—	42·00	34	34	49
9	,,	,,	—	49·00	23	23	25

Up to 8 cycles, total cryolite recovered	...	408 gm
Boric acid in spent liquor	...	64 gm
Loss of boric acid	...	11 gm
Boric acid loss/100 gm of cryolite	...	2·7 gm
Total fluorine in 800 gm of fluorspar	...	329 gm
Up to 8 cycles fluorine recovered	...	212·2 gm
Overall recovery	...	64·51 %

TABLE III Cyclic process for the preparation of cryolite by fluoboric acid method.

Cyclic experiment 3

Solution volume	...	500 c.c.
Sodium sulphate	...	25 gm
Temperature of leaching	...	95°C
Time	...	2 hours

No. of cycle	Fluorspar (gm)	Sulphuric acid	Boric acid (gm)	Residual H_2SO_4 (gm)	Sodium carbonate (gm)	Hydrated alumina (gm)	Cryolite obtained (gm)
1	100	Theoretical	60	1·0	38	38	72
2	,,	,,	—	5·84	35·6	35·6	68
3	,,	,,	—	7·40	34·7	34·7	62
4	,,	,,	—	11·68	35·3	35·3	64
5	,,	,,	—	12·26	36·0	36·0	60
6	,,	,,	—	23·36	32·0	32·0	48
Purified							
7	,,	,,	—	12·26	31·5	31·5	42
8	,,	,,	8	36·80	30	30	49
9	,,	,,	—	46·00	28	28	30

Total cryolite obtained	...	465 gm
Boric acid in spent liquor	...	59 gm
Loss of boric acid	...	9 gm
Boric acid loss/103 gm of cryolite	...	1·93 gm
Total fluorine in 800 gm of fluorspar	...	329 gm
Fluorine recovered	..	241·3 gm
Overall recovery	...	73·5 %

To find out the cause of retardation of the reaction between calcium fluoride, boric acid and sulphuric acid, leaching experiments were carried out in the presence of compounds added to the otherwise normal solutions. The results of such experiments are shown in Table IV.

Aluminium fluoride suppresses the reaction as its quantity increases in the liquor. Its concentration must be kept as low as possible. Ferric sulphate and ferrous sulphate each equal to five grammes of iron did not affect the reaction adversely. But sodium sulphate did affect the reaction adversely at very high concentrations such as 200 gm/litre. So it should not be allowed to build up in the liquor to that extent. The conclusion drawn from these

rity except Al ions does not affect the leaching reaction adversely to the extent as was shown in the cyclic experiments. There must be the combined effect of the impurities, which is responsible for the inhibition of the reaction. To obtain the best results the process must be controlled to an extent so that all these compounds are kept as low as possible in the process liquor.

The overall fluorine recovery obtained is better with a pure grade of fluorspar. The cryolite produced conformed to standard specifications laid down by the aluminium industry. The average chemical analysis is shown along with the specification of cryolite for aluminium production in Table V.

TABLE IV Effect of impurities on fluorine extraction.

Solution volume	...	500 c.c.
Boric acid added	...	55 gm
Sodium sulphate added	...	25 gm
Time of leaching	...	2 hours
Temp. of leaching	...	95±2°C

Serial No.	Amount of fluorspar (gm)	Amount of H_2SO_4	Impurity added	Amount of impurity added (gm)	Fluorine in fluorspar (gm)	Fluorine leached (gm)	Fluorine % leached
1	90 (Acid grade)	Theoretical	—	—	43	42·14	98
2	,,	,,	AlF_3	6·3	43	38·9	90·4
3	,,	,,	,,	12·7	43	32·5	75.5
4	,,	,,	,,	19·0	43	30·75	71·5
5	,,	,,	$Fe_2(SO_4)_3$	18·0	43	40·9	95·1
6	100 (Met. grade)	,,	$FeSO_4$	13·6.	41·1	38·9	94·9
7	,,	,,	Na_2SO_4	75	41·1	36·8	89·6

TABLE V Analysis and specification of cryolite

Radicals	N.M.L. cryolite average anlysis	Cryolite suitable to Aluminium industry
P_2O_5	0·05 to 0·08%	Not more than 0·1%
SiO_2	0·1 to 0·2%	,, 0·6%
Fe_2O_3	0·03 to 0·06%	,, 0·25%
SO_3	1·4 to 3·0%	,, 5·0%
Ca	0 5 to 0·6%	
Na	22 to 28%	
Al	17 to 19%	
F	49 to 55%	

Acknowledgement

The authors' thanks are due to Dr B. R. Nijhawan, Director, National Metallurgical Laboratory for his kind interest in the work. Thanks are also due to Dr T. Banerjee, Scientist, National Metallurgical Laboratory for his valuable suggestions during the period of this investigation.

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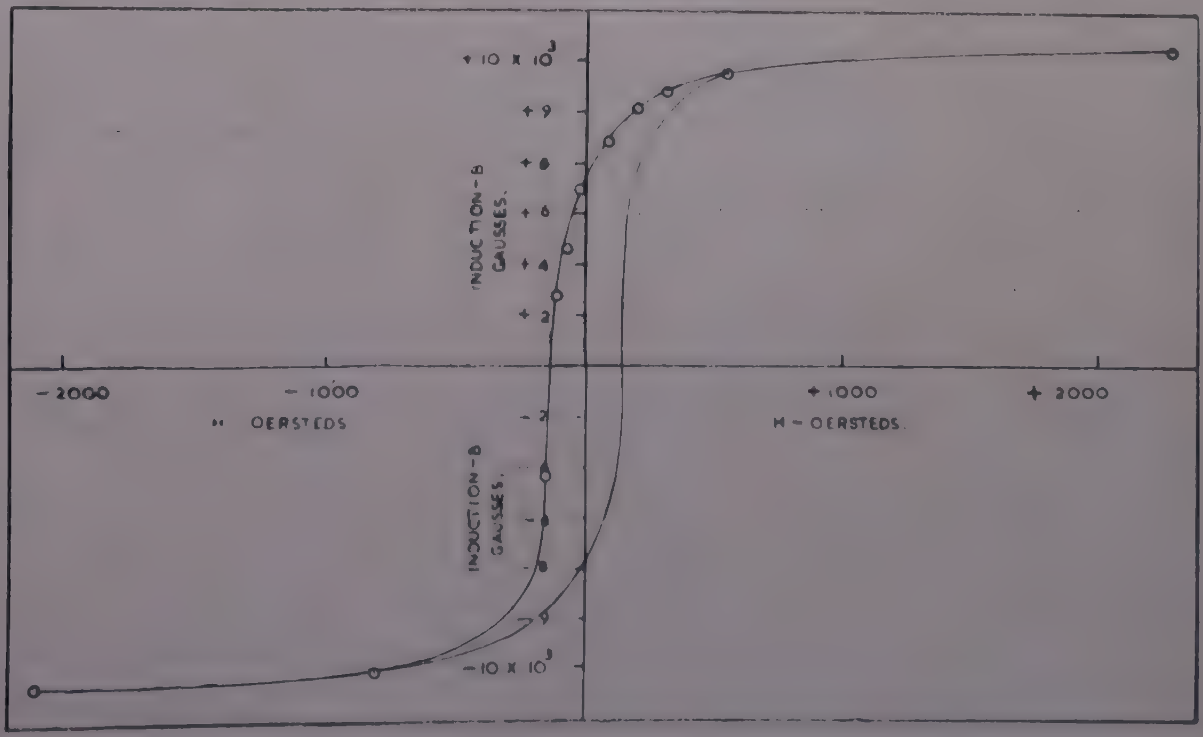
Perminvar Effects in Some Alnico Magnets

Ved Prakash
C. R. Tewari
B. R. Nijhawan

ELMEN[1] has shown that unusual magnetic properties resulted after suitable heat-treatment of Perminvar type alloys containing nickel-iron and cobalt. Slow cooling of such alloys through a narrow temperature range or their continuous heating for a long time at a lower temperature resulted in their hysteresis loop being constricted in the second part of the quadrant. Recently Kaya[2] has shown that constricted hysteresis loops also occur in Permalloys near Ni_3Fe composition under conditions which promote limited order (short range). The quenched or well-annealed alloys showed normal loops. Such loops have so far been observed for soft magnetic materials only which can be magnetized or demagnetized in small fields and their magnetization normally proceeds through movement of domain boundaries.

Recently, while the authors were studying the heat-treatment of Alnico magnets in relation to their chemical compositions, it was observed that an Alcomax alloy specimen of composition Ni 13·2%, Al 9·9%, Cu 3·1%, Co 22·3%, Fe balance, when cooled from 1 300 to 600°C in a magnetic field of 1 700 oersteds and tempered at 600°C, gave hysteresis loop which had a constriction in the second quadrant of the B.-H. curve Fig. 1b). The Alcomax specimen, was a cylindrical rod of (L/D ratio 20, and tested ballistically for its hysteresis loop by using a solenoid as a source of magnetic field up to 3 000 oersteds. The constriction in the hysteresis loop was very much similar to the one reported by Elmen in his Perminvar alloys or by Kaya in Permalloy composition near Ni_3Fe. The constriction in the loop of the Alnico alloy under reference was absent when tested after critically cooling as above (Fig. 1a) and appeared only after tempering at 600°C (Figs. 1b, 1c). It is the object of this Note to report that constricted loops can also occur in permanent magnet alloys which require high field for their induction to reach the saturation value and are amenable to heat-treatment in a magnetic field.



(a) Normal hysteresis loop after cooling in a magnetic field at a rate of 8·1°C/second from 1 300° to 600°C.

The constriction in the loops of soft magnetic materials has been explained on the basis of ordering and direction order theories[1-3] which envisage that

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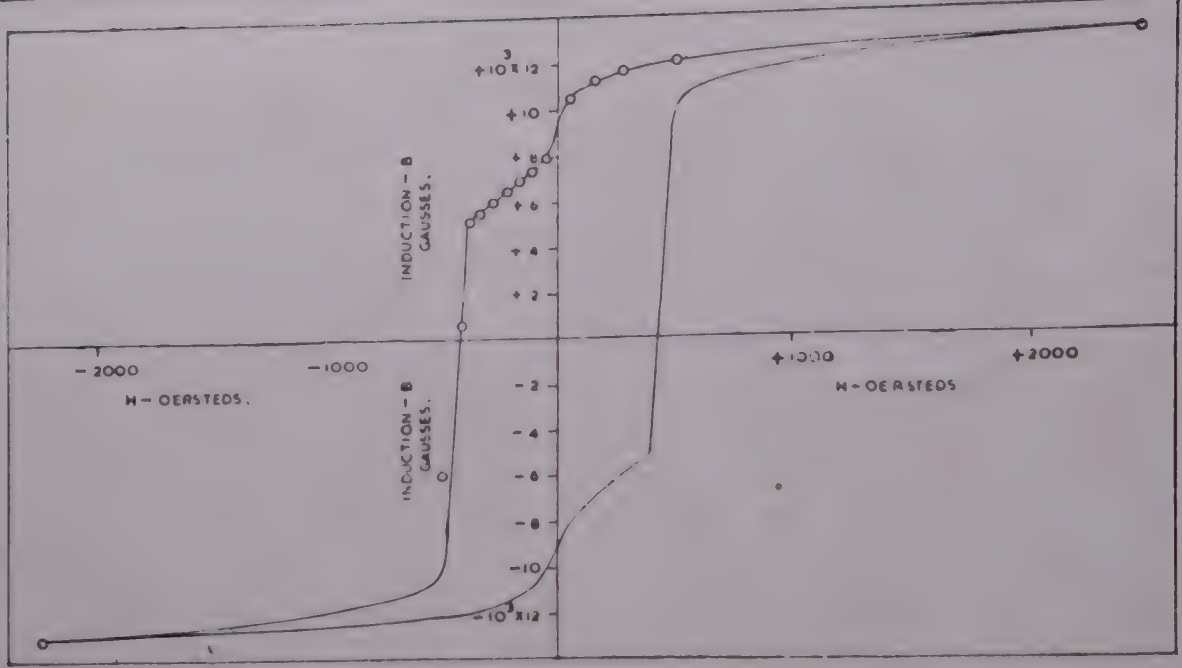
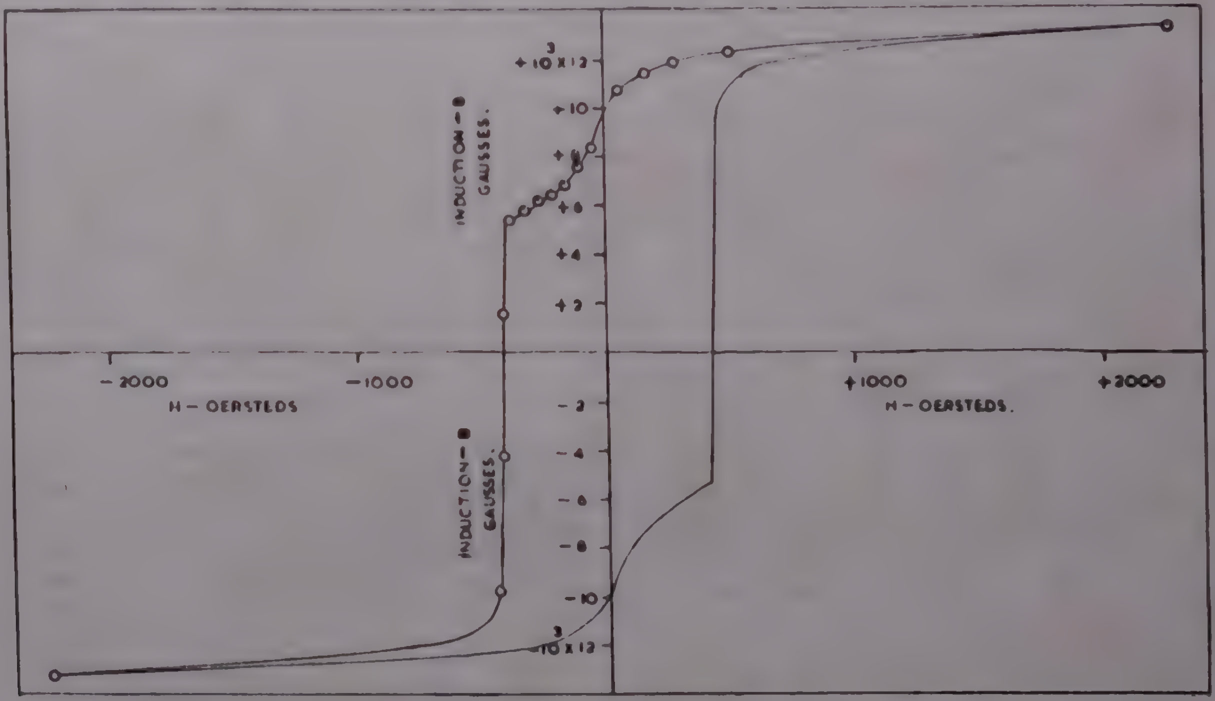
Dr Ved Prakash and Mr C. R. Tewari, Scientists, and Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, Jamshedpur. *Manuscript received on the 5th February, 1965.*



(b) Showing constriction in the loop after 3 hours of tempering at 600°C after cooling as (a).



(c) Same as (a) but the alloy tempered for 6 hours at 600°C.

1 *Hysteresis loops of Alcomax type alloy showing constriction.*

hysteresis loops of peculiar shapes can result from a mixture of two magnetic materials in a single sample. These ideas can be extended to explain constriction in the high cobalt Alcomax type alloy under discussion. Clegg and McCaig[4] have recently investigated Alcomax III alloy, which is similar to alloy No. 8 and observed two kinks in the magnetization curves after different heat-treatments, indicating the presence of two ferro-magnetic phases with different Curie points. The phase with a high Curie point develops uniaxial anisotropy during magnetic annealing while the phase with a lower Curie point, which nucleates during tempering, does not develop uniaxial anisotropy. The high Curie point phase with uniaxial anisotropy will lead to high value of remanence and coercive force as compared with the low temperature Curie point phase. The net effect of these two phases possessing different magnetic properties will be to give an average demagnetization curve, the shape of which will depend upon the mode of magnetization and contribution to magnetic properties of each phase.

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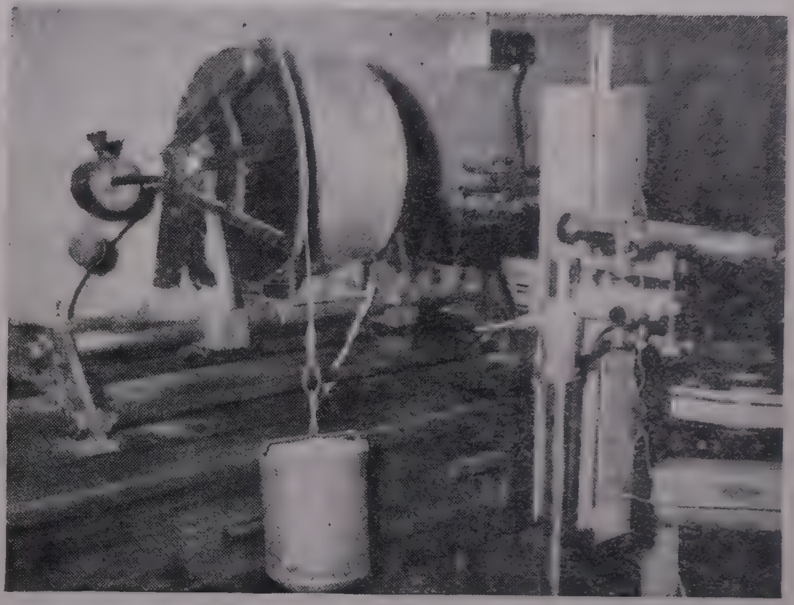
Studies on Mechanical Properties of Refractories at High Temperatures

T. V. Prasad

REFRACTORY materials used as structural components in high temperature industrial furnaces are subjected to severe external and internal stresses during service. As such their high temperature mechanical properties, particularly their ability to withstand loads at high temperatures, are important factors in determining their choice and applications. An understanding of the mechanical properties and behaviour of refractories at high temperatures is highly important and work thereon has led to the development of improved refractories, such as direct bonded basic brick successfully used in open hearth furnace roofs. There is comparatively little work done in India on this subject. Keeping in view the importance of the subject, work was taken up at the National Metallurgical Laboratory on correlation of high temperature mechanical properties of some basic refractories with their constitution and structure. An apparatus for study of creep in refractories under torsion has been designed and fabricated at the National Metallurgical Laboratory. Studies on the subject employing this apparatus, possibly the first of its kind in this country, will throw useful light on the nature and behaviour of Indian refractory materials at high service temperatures.



Apparatus for study of creep in refractories under torsion designed and fabricated at the National Metallurgical Laboratory.

Mr T. V. Prasad, Scientist, National Metallurgical Laboratory, Jamshedpur.

Notes and news

HOME NEWS

Three State sector steel units maintain production

The three steel plants in the public sector have maintained production at or about their rated capacity level during the month of August, 1965.

Bhilai : The Bhilai steel works produced 121 500 tonnes of ingot steel during the month, which was the highest production recorded in any month so far. This included 36 177 tonnes of ingot steel produced by two 500-tonne open hearth furnaces. Production of pig iron (hot metal) totalled 141 374 tonnes, including 58 257 tonnes from the fourth blast furnace. These figures were also the highest for any month so far. The rolling mill of the steel works rolled 98 083 tonnes of steel ingots. Production of blooms and slabs was 85 270 tonnes, of billets 47 688 tonnes, of rails and structurals 35 247 tonnes.

Rourkela : During the period, production in all the units of the Rourkela steel plant was maintained above the rated capacity level. Tinning lines established a new record with the production of 2 862 tonnes of tin plates as against the previous best performance of 2 712 tonnes obtained during July last. Coke ovens produced 104 600 tonnes of coke during the month, representing nearly 105 per cent of the rated capacity of the plant. Production of hot metal from the three blast furnaces amounted to 93 857 tonnes. Steel ingot production totalled 95 142 tonnes which is equivalent to 114 per cent of the rated capacity of the plant. The blooming and slabbing mill rolled 99 570 tonnes of ingots into 82 374 tonnes of slabs during August. The performance of the mill during the month was higher than the rated capacity by nearly 19 per cent. The plate mill produced 14 558 tonnes of plates during August as against a monthly rated capacity of 14 200 tonnes, the performance during August being nearly two per cent higher than the rated capacity of the mill. Production of hot rolled coils in the hot strip mill totalled to 58 175 tonnes as against 57 486 tonnes obtained during July. The performance of the mill is nearly 16 per cent higher than the rated capacity of the mill. Production of cold rolled strips increased from 17 059 tonnes in July to 19 833 tonnes in August, which is equal to the monthly rated capacity of the mill. Finished steel production totalled to 66 234 tonnes during the month, which is nearly 6 200 tonnes more than the rated capacity of the plant and is equivalent to 110 per cent of the rated capacity. Despatch of finished steel amounted to 66 566 tonnes and total despatches of all products were 86 393 tonnes.

Durgapur : Seven major units of the Durgapur steel plant out of nine produced at or about the rated capacity during August, i.e., coke ovens (14 per cent), the blast furnace (101 per cent), the steel melting shop (100 per cent), the blooming mill (101 per cent), the billet mill (103 per cent) and the sleeper plant (100 per cent). The merchant mill broke all previous records and produced 32 181 tonnes of merchant sections during the month as against the previous best of 30 849 tonnes attained in February, 1965.

Financial Express, 6.9.65.

Record TISCO output

The operation of the Tata Iron and Steel Co. Ltd., for the year ended March 31, 1965, has resulted in a record production of 1·568 million tonnes of saleable steel. Over the year the production of iron has gone up from 1·809 million tonnes to 1·885 million tonnes, steel ingots from 1·892 to 1·956 million tonnes and saleable steel from 1·507 to 1·568 million tonnes, representing an increase of 4·2 per cent, 3·38 per cent and 4·05 per cent respectively. The ratio of finished steel products to the total output of saleable steel has improved from 68·7 per cent to 70·7 per cent. With the co-operation and assistance of railways, the company has been able to effect record despatches totalling 1·546 million tonnes compared with 1·467 million tonnes in the previous year. The shipment of steel against export orders during the year has accounted for 10·895 tonnes.

Hindusthan Times, 4.8.65.

Russia to help build sixth Bhilai furnace

The sixth blast furnace at Bhilai which will be constructed with Soviet assistance is expected to go into production in 1967. The agreement for the construction of the sixth blast furnace will be signed between Hindustan Steel Limited and the Soviet organisation "Tiazpromexport" at Ranchi. The blast furnace will have an annual output of 5 00 000 tonnes of pig iron. The Soviet experts revealed that the designing of the sixth blast furnace had been, to a large extent, done by Indian engineers. Another distinguishing feature in its construction is the greater utilisation of indigenous supplies of equipment. At the end of the Third Five Year Plan, the Bhilai Plant will be producing 25 per cent of the country's steel and 40 per cent of the production in the Public Sector

Amrita Bazar Patrika, 3.8.65.

New company to build Bokaro

A new Government company, Hindustan Steel Construction Limited, has been formed to do all the civil engineering works of the Steel Ministry. The company, formed with a capital of Rs 10 000 000 will have a work force of some 3 000 engineers and supervisory staff. The immediate task of the new company is to do the excavation and construction jobs at Bokaro for the Russian-assisted steel plant there. Experts reckon that even the first phase of the construction job will entail contracts worth Rs 220 000 000. This includes building of houses at the Bokaro township. The schedule for the Bokaro plant is very tight. Pig iron is expected to be produced from its blast furnaces by the end of 1968 and rolled products are to be manufactured in 1969. Soviet equipment for excavating the site for the plant has already begun to arrive. So have Russian experts.

Amrita Bazar Patrika, 2.8.65.

Tata Steel asked to expand output

The Tata Iron and Steel Company has been asked by the Government to consider an expansion of about 2 million ingot tons in the Fourth Plan period.

Indian Express, 1.8.65.

16·5 million tonnes steel output by Fourth Plan-end

India had a tentative target of producing 16·5 million tonnes steel by the end of the Fourth Plan but in spite of this ambitious target it would be required to import certain qualities of steel. Export of three lakh tonnes this year would bring India foreign exchange of nearly Rs 12 crores at the rate of Rs 400 per tonne.

Hindustan Times, 6.8.65.

Steel production costs : study team announced

The Government has decided to constitute a committee to study the cost of steel production. The Government has been concerned for some time past about the rising cost of production of steel and has had under consideration the appointment of a committee to examine this matter in detail, analyse all the factors going into the cost, assess the reasons for the increases and advise the Government on the measures necessary to reduce it. The committee will submit its report in four months' time.

Hindu, 30.8.65.

Locating sources of non-ferrous metals

A massive bid is proposed to be made during the Fourth Plan to locate indigenous sources of non-ferrous metals, which are most scarce in the country. As part of this programme, 40 to 50 per cent of the capacity of the Geological Survey of India (GSI) and the Indian Bureau of Mines (IBM) would be utilised in the search for and proving of non-ferrous metal deposits. These investigations are likely to test, to a large extent, the potentiality of the country for production of non-ferrous metals and the established deposits of economic importance which would be exploited in the Fifth Plan. Negotiations with Canada for the supply of drilling and other equipment worth nearly Rs 5 crores for GSI and IBM have reached an advanced stage. Meanwhile, preparations are being made for the first flight, which is likely to commence in October under 'operation hard rock' for an aero-magnetic survey for non-ferrous metal deposits.

Financial Express, 6.9.65.

Mineral production shows 6 per cent rise in 1965

The total value of mineral production in India, excluding Goa, during April this year was Rs 203 million as against Rs 199 million in the previous month, showing an increase of 2 per cent according to the estimates made by the Indian Bureau of Mines. This excludes the value of petroleum, minor mineral and minerals declared as prescribed substances under the Atomic Energy Act, 1948.

Also, the total value recorded in the first four months of 1965 was higher at Rs 763 million in comparison with Rs 717 million in the corresponding period of the previous year, registering an increase of about 6·4 per cent. Coal and lignite with an output of 5·76 million tonnes and 211 000 tonnes respectively constituted the leading group. Next to coal and lignite, among the principal minerals in the ferrous group, the production of chromite was 8 690 tonnes, iron ore 1·24 million tonnes and manganese ore 119 000 tonnes. In the non-ferrous group, the production of bauxite was 66 000 tonnes, copper ore 38 392 tonnes, gold 360 kilograms, silver 393 kilograms, ilmenite 2 587 tonnes, lead concentrates 531 tonnes and zinc concentrates 881 tonnes.

The output of principal non-metallic minerals was : asbestos 342 tonnes, dolomite 78 000 tonnes, gypsum 111 000 tonnes, kyanite 2 272 tonnes, limestone 1·66 million tonnes, magnesite 18 975 tonnes, mica 1 909 tonnes and salt 756 000 tonnes.

Hindustan Times, 18.8.65.

Big private sector aluminium plant likely in Kerala

A Rs 22-crore aluminium plant is likely to be set up in Kerala in the private sector. The proposal was discussed by the representative of a leading Indian concern with the State Industries Secretary. The concern has already obtained a licence for setting up a plant with a production capacity of 30 000 tonnes per annum in Kerala. The plant would be commissioned within two years of commencement of work of putting up the factory.

Hindu, 30.8.65.

Aluminium plant in Belgaum district

The construction of the aluminium ingot plant in the private sector will begin soon in Belgaum district. The plant will have an initial ontlay of Rs 30 crores and an ultimate capital of Rs 100 crores. Bulk power will be made available to the plant from the Sharavathi hydel project and bauxite will come from Maharashtra.

Times of India, 28.8.65.

Bauxite deposits at Kodai Hills : scope for aluminium unit in Madurai

Good deposits of bauxite, the quality of which is definitely superior to that of Salem, have been reported from the Kodai Hills. The content of aluminium in the bauxite ore at Salem is 42 per cent, the content of aluminium at Kodai Hills is 48 to 52 per cent, and the total quantity available is estimated at about 2 million tons.

Economic Times, 14.8.65.

4·9% rise in per capita income

The Central Statistical Organization in its provisional report on national income said that the average annual increase in real income during the first four years of the Third Plan was 4·1%. During this period the average annual increase was 2·3% in agriculture, 7·4% in mining and factory establishments, 4·5% in transport and communications and 6·0% in the remaining sectors. The per capita national income in real terms increased by 4·9% during 1964-65, the average annual increase during the first four years of the Third Plan being 1·8%. The contributions of individual sectors to overall percentage change in real income during 1964-65 are given below :

Sector	Percentage contribution to total national income in 1963-64.	Percentage change in 1964-65 over 1963-64	Contribution to the overall percentage change in 1964-65 over 1963-64.
Agriculture (proper)	35·9	10·2	3·7
Mining and Factory Estt.	10·5	5·9	0·6
Communications	0·6	13·0	0·1
Railways	2·7	2·9	0·1
Organized Banking and Insurance	1·2	7·4	0·1
Commerce and Transport	15·4	5·9	0·9
Others	33·7	5·6	1·9
All sectors	100·0	7·3	7·3

The following table presents the estimates of national income and per capita income at 1948-49 prices for the years 1950-51, 1955-56 and 1960-61 to 1964-65.

Year	National income at 1948-49 prices (Rs 100 crores)	Per capita income (in rupees) at 1948-49 prices (based on 1941, 1951 and 1961 population census figures).
1950-51	88·5	247·5
1955-56	104·8	267·8
1960-61	127·3	293·2
1961-62	130·6	294·3
1962-63	133·1	293·4
1963-64	139·1	299·8
1964-65	149·3	314·4

Statesman, 27.8.65.

Fourth Plan to be defence-oriented

While approving an outlay of Rs 21 500 crores for the Fourth Plan, the National Development Council today authorised its Chairman, the Prime Minister, Mr Shastri, to alter, amend and make all necessary changes in the Plan to make it defence-oriented. The Council's resolution emphasised that, at this time, when the country was engaged in meeting the challenge of serious external threats and had to undertake massive efforts for development, the nation would rise to the occasion and demonstrate its inherent strength and solidarity.

Some of the sectoral allocations suggested were : Agriculture—Rs 2 372 crores in public sector and Rs 7 000 crores in private sector; irrigation—Rs 924 crores in public sector; power—Rs 1 826 crores in public and Rs 50 crores in private sector; small industry—Rs 395 crores in public and Rs 400 crores in private sector; organised industry—Rs 2 886 crores in public and Rs 2 400 crores in p
nications—Rs 2786 crores in public sector and Rs 650 crores in private sector; education—Rs 1 260 crores in public and Rs 100 crores in private sector ; scientific research—Rs 148 crores in public sector; health—Rs 578 crores in public sector; water supply—Rs 371 crores in public sector.

Hindusthan Standard, 7.9.65.

OVERSEAS DIARY

Soviet steel units produce more than Plan targets

The Soviet iron and steel industry successfully achieved the plan targets for the first half of 1965 and produced more pig iron, steel and rolled sections above the target figures.

The iron and steel industry has been developing at a rapid pace during all the years of the Seven-Year Plan from 1959 to 1965. Within that time 17 blast furnaces have been built at different works. The Soviet Union, for the first time, started building blast furnaces with a volume of 2 000 cubic metres.

A tendency to increase the output capacities of installations was observed in the steelmaking industry. Open hearth furnaces with volumes of 500 and more tons were built. But the most remarkable feature of technological progress in the steel industry during the past few years was the convertor method of steel-smelting. The number of operating convertors will be augmented this year by five more powerful units going up in the Ukraine and the centre of the European part of Russia.

Economic Times, July, 1965.

Rolling of special steels

The Societe Des Forges et Laminoirs, Jemappes, has commissioned a two-high reversible 750 mm blooming mill, particularly adapted for the rolling of special steels. This equipment has a monthly production capacity of 15 000 tons.

The installed capacity thus represents 8 000 h.p., shared among 200 engines. Only one operator is required. The improvements to the assembly, range from fully-controlled adjustment by transistorised drives, photoelectric cells, industrial television and servomechanisms, to a punched-card programming device, as well as the drive of the main engine by mercury vapour arc rectifiers and of auxiliary engines by silicon rectifiers.

Indian Engineering Association News Bulletin, April, 1965.

Research into production of sheet steel from powder

Research into the production of sheet steel from a powder, which could bring important economies to steelmaking, has begun at the Birmingham College of Advanced Technology in England.

The research is being financed by the British Iron and Steel Research Association and the Science Research Council. Experimental work has already been conducted in several places on the possibility of metal strip formation from powder, but not of non-ferrous metals. The major problem on which research will concentrate now is to find, if it is possible, to produce a pure enough iron powder from which steel could be manufactured. If this problem is satisfactorily solved, the result could bring considerable economies in sheet steel production, affecting many industries.

British Information Service, BF 732, p. 32

Kobe Steel's new wire mill

Kobe Steel completed the first stage of construction of the new second wire rod plant (No. 6 wire rod mill) at its Kobe Works and put it into partial operation in June, 1965. The construction had been underway since July 1964 as part of the company's third expansion and modernization programme.

The newly completed wire rod mill has for the present a monthly production capacity of 7 500 tons of special wire rods, mainly low alloy steel wire rods to be increased eventually to 15 000 tons when the whole construction work for the mill is completed in September, 1966. The mill, whose rolling machine proper and main ancillary equipment were all designed and manufactured by the company's Machinery Division, is claimed to be the most advanced of its type of mill in the world, with such advantages as follows : A final rolling speed of 35 metres per second ; ability to produce wire rods of high dimensional precision because of the continuous rolling and loop control ; the adoption of movable hearth-type heating furnaces especially steel suited for special steels; and provision of wire cooling equipment to increase the wire drawing of high carbon steel.

Far East Iron & Steel Trade Reports, No. 127 Aug. '65

Yawata to manufacture LD converters for BHP

Yawata Steel Co. recently reached an agreement with the Broken Hill Proprietary Co., the largest steel company in Australia, for its manufacture of two LD converters for the latter. The Machinery & Engineering Division of Yawata has already started manufacturing the converters for completion next February. This will be the first of such exports from Japan. The two coverters will be installed at the Newcastle works of the Australian steel firm.

Far East Iron & Steel Trade Reports, No. 127, Aug. '65.

Colour-coated sheets

Dorman Long (Steel) Ltd. is producing galvanised steel sheets colour-coated with *pvc*. This new material marketed under the name 'Colour steel' is available with a variety of attractive colour coatings applied to either one or both sides of the sheet. This development is the result of an extensive research programme.

When colour-coated on one side only, the new sheet is ideal for many applications such as decking sheets in insulated roofing in which the galvanised side is either covered or not exposed to abnormally corrosive condition. The sheets are manufactured in a range of profiles for both cladding and decking applications. Flat sheets are also available up to 1/8 in. wide and the length up to 20 ft.

British Steel Maker, June, 1965.

Recent developments

Continuous degassing speeds output of high alloy steels

Trials with a continuous, vacuum degassing unit in the production af high alloy steels have indicated the process can be used to increase steelmaking productivity, reports the British Iron & Steel Research Association (BISRA).

Both laboratory and pilot plant trials have shown that it is possible to operate the continuous process in a unit where chamber size is not greatly dependent on the quantity of steel to be treated, says BISRA. By contrast, batch type degassing requires large vacuum chambers if large quantities are to be processed. Even with poor vacuum conditions, hydrogen can be removed satisfactorily, the Association says.

BISRA made its report on the basis of 54 trials completed with a unit installed at Low Moor Alloy Steelworks Ltd., Bradford, England, extending over an operational period of 40 weeks. Of that number of trials, 37 were termed substantially successful. Twelve consecutive heats were degassed without failure.

Commercial development started in 1963 at Low Moor and the first cast was made there in September, 1963.

Process : Basically, the BISRA process consists of pouring molten metal into an inlet tundish from which it is drawn into a vacuum chamber, where it is degassed and poured out into another tundish via a barometric seal. The degassed steel can then be cast directly into ingots or collected in a ladle for subsequent teeming by conventional means or continuous casting.

Before the metal is teemed into the inlet tundish, the refractories in the units are heated to the highest practicable temperature. Glass is melted in the tundish under the outlet pipe and the tundish raised to press firmly against the open end of the pipe so that the glass forms a vacuumtight seal until the process is started.

When preheating has been completed, the burners are turned off, the flue opening sealed, and the chamber evacuated as rapidly as possible. As soon as the inlet tundish is full of metal, it is raised, breaking the mild steel rupture disc temporarily sealing the inlet pipe. The metal explodes into droplets as it is drawn into the vacuum chamber.

When sufficient metal has been admitted to fill the outlet pipe and forms a shallow pool in the hearth, the seal in the outlet tundish is broken. Because the weight of metal in the outlet pipe is greater than can be supported by atmospheric pressure, the metal is not drawn back into the vacuum chamber but is discharged into the tundish in a continuous flow until all of the available metal has been used. Nitrogen is then admitted into the chamber to expel any remaining metal and restore the pressure to atmospheric without the risk of explosion.

Alloys worked : Most of the work at Low Moor has been concentrated on the ladle degassing of high chromium steels with specifications comparable to the 300 and 400 stainless series in the U.S., and a high carbon chrome tool steel, in 2½ and 5 ton heats.

BISRA reports that while heat losses during the trials have been high, it hopes to reduce them as the scale of operations increases. Observation of heat losses indicates, says BISRA, that while the overall value is high, the temperature loss in the degassing plant itself is relatively small. It reports average hydrogen removal has been about 5o per cent at an operating pressure in the region of $1{\cdot}6^{-10}$ torr. An average loss of 14 per cent manganese was recorded, but no significant change in oxygen or nitrogen content was noted, say the researchers.

Modifications : As a result of the trials, modified steelmaking techniques have been evolved and examined during development of the BISRA process. It has been found, except for very low carbon, high chromium steels, that by suitable selection of the charge, oxygen injection can be eliminated and degassing substituted, in effect, for the carbon boil, the Association reports. In this way, the steel is virtually made under a reducing slag without overheating, thereby keeping both the slag and steel in good condition, and in consequence, productivity can be greatly increased.

Steel, July 5, 1965.

Anti-corrosion product

A number of advantages are claimed for a new anti-corrosion product, 'Rustal' tablets over conventional methods which rely on vapour-phase inhibitors to provide protection. The tablets are said to be unique in their clean, simple and instant-acting operation and to eliminate entirely the need for dessicants, greasing, dipping, spraying or coating. The use of 'Rustals' provides an improved method of packaging, since the articles to be protected can simply be inserted with a tablet in a container, without any need to warp them in specially treated papers.

The tablets can be used for long term (up to 15 years) protection in storage, for preventing corrosion during temporary plant shut-downs, for simple protection of mass produced items, and for many other applications where simple control of corrosion is required. 'Rustal' tablets are available in four sizes to protect the contents of container up to 400 cu. in. in volume.

Metallurgia (72), 429, July 1965.

Slagceram—a new constructional material

Slagceram is a new material under development by the Iron-Making Division and the Chemistry

Department of the British Iron & Steel Research Association. Its basic constituent is blast-furnace slag. Slagceram is a microcrystalline material produced by the devitrification of a crude glass made from metallurgical slag and consists essentially of 45 to 65 per cent SiO_2, 15 to 45 per cent CaO, 5 to 30 per cent Al_2O_3, up to 10 per cent MgO, and an effective amount of nucleating agent. In practice, this composition is achieved by adding sand and the nucleating agent to molten or solid slag. It has been shown that the oxides of transition elements such as vanadium, chromium, titanium, and iron, as well as some fluorides and phosphates, are effective in promoting nucleation.

Raw materials

Most blast-furnace slags in the solid or liquid state may be used to make slagceram or 'Vitroslag', although it is obviously preferable to utilize the heat already present in molten slag and thereby save fuel during the melting operation. There is a similar flexibility in the choice of sand employed which can be added cold or preheated. The choice of nucleating agent depends upon the furnace atmosphere prevailing during melting.

Melting

During the melting sequence, the three components, i.e. slag, sand and nucleating agent, are heated until a homogeneous liquid is formed. Static or rotating furnaces may be used and a process has been developed involving the use of both. When slagceram is made in a static furnace, mixing is promoted by the convection currents within the molten bath and by the use of mechanical aids. If a rotating furnace is used, mixing promoted by the rotation and a homogeneous solution is produced more quickly. However, material direct from a rotating furnace tends to contain many bubbles and a short settling treatment in a static furnace is necessary if a dense product is required. The rotating furnace alone has been used to make lightweight slagcerams.

Forming

The finally shaped object is produced directly from the melt and the methods used to form the material are similar to those used in making glassware. Casting in sand moulds and metal moulds has been developed and such techniques are useful when complex shapes in limited quantity are required. Casting into sectional moulds may be used when simple shapes are required in larger numbers. Slagcream is ideally suited to a pressing operation which has the advantage that fairly complex shapes may be made in large numbers with relatively simple equipment. This process is well established in the glass industries and can be successfully automated, if required. Preliminary experiments have been carried out to investigate the possibility of rolling slagceram. The type of surface finish on the final product is largely governed by the forming operation and casting in metal moulds or pressing is used when smooth surfaces with features in low relief are required

Heat treatment

The formed articles are passed into a heat-treatment furnace where they are subjected to a treatment which develops crystallinity. This is a multi-stage treatment consisting of nucleation at a temperature slightly above the annealing point followed by crystallization at a higher temperature. During nucleation sub-microscopic nuclei are formed, which develop into crystals during further heating. The rate of temperature increase between the nucleation and crystallization temperatures is important and control is necessary to ensure that the developing crystals form a skeleton framework within the material and counteract the effects of rising temperature.

Fine and coarse grained material can be produced by varying the details of the thermal cycle, the desired crystal size being dependent on the proposed application.

Finishing processes

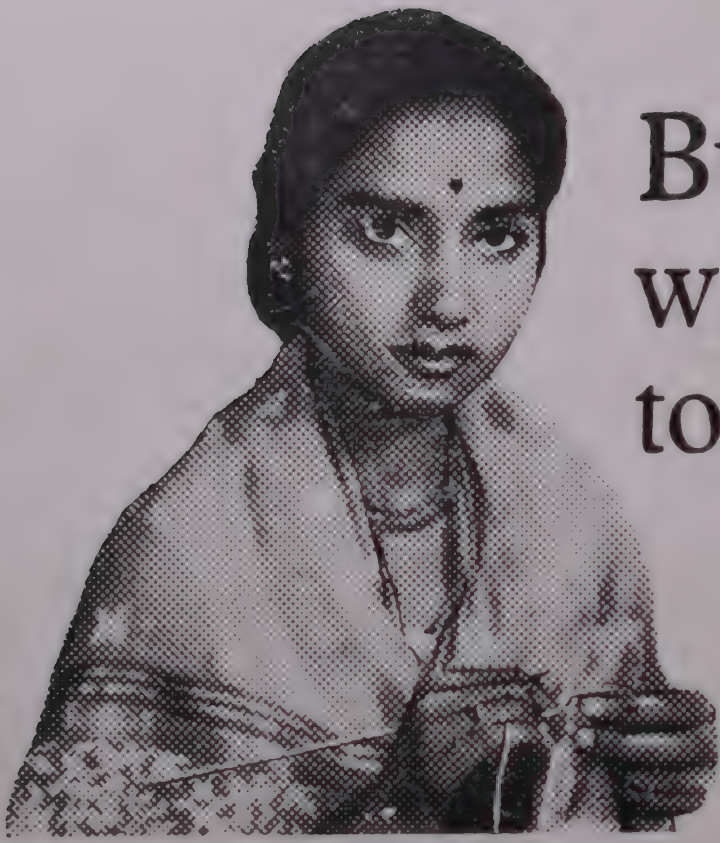
Slagceram can be used directly after crystallization, and no further treatment will be necessary for most products. Some applications, however, may require a different surface appearance and techniques have been developed which enable the surface to be polished or vitreous enamelled. Polishing is carried out by grinding the material with different grades of abrasive powder and is comparable with the process used to polish granite. Slagceram can be cut by a diamond-edged saw, though it is obviously desirable to make the final shape, complete with holes and appendages, at the forming stage before heat treatment. Ths vitreous enamelling process is well established and slagceram can be successfully enamelled using the standard practice. The enamel can be applied before heat treatment and it is possible to incorporate the heat-treatment cycle with the enamelling cycle and thereby save firing costs.

Application of slagceram

The properties of slagcream make it versatile material suitable for many applications both decorative and useful. High strength, hardness, and abrasion resistance are its main characteristics enabling it to be used for many building purposes. Economic assessments have shown that the process is economically viable and that the final products should be competitively priced.

Potential of slagceram

It is apparent from the researches carried out that only the fringes of this new technology have been explored and that the scope of potential developments is immense. Compositional changes and alterations in thermal treatment will enable a range of slagceram to be made: each with its own individual properties and texture. Experiments are being carried out to develop slagcerams of different bulk colour and new methods of forming are under constant review. Further research will undoubtedly reduce the present costs of producing the material and as the understanding of the basic phenomena increases, so will the range of applications.



But what can I do to help?

There is so much that every Indian woman can do, *now*, to strengthen and defend the Home Front. Take part in Defence through local women's organisations. There is plenty to be done. Contribute, and encourage contribution, to National Defence Fund and buy Defence Certificates. There are, too, the many personal efforts you can make—in discipline, behaviour and attitude :

- *Wage war on waste; check thoughtless buying and resist inflated prices.*
- *Do not buy gold. Give your gold for country's cause.*
- *Be resolute in work, whatever it may be, because each task done just that little more efficiently helps the national drive, strengthens India's position.*
- *Rouse yourself from apathy, and Take Action.*

BE VIGILANT

—take part in national preparedness

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THE CHANGING

Kulti. Neighbour to a steel town. Precursor of a proud tradition. It all really began at Kulti way back in 1870. Here was the oldest successful unit in India producing pig iron by modern methods. With production upgraded at Burnpur the blast furnaces closed down in 1958. But obsolescence never overtook Kulti. Its integrated iron, steel and non-ferrous castings foundry is still one of the largest in the East—the spun pipe foundry one of the best. Kulti's present consumption of pig iron exceeds 20% of that for the whole of India; it can, in fact, take in more, if available.

Thus Kulti continues in a career of planned growth. Serving Burnpur, serving other steel plants—and India's railways, chemical and sugar industries with complicated castings. Spinning out pipes as well by full train loads for the projects and utilities as no other unit does. And Kulti today is confident of adding on to its achievements

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NML TECHNICAL JOURNAL

VOL. VII No. 4 NOVEMBER 1965

Indian Metallurgists and the Present Emergency

THE impact of modern technological development has been square and everlasting on Indian metallurgical industries. The problems that confront India are complex, relating chiefly to difficulties of foreign exchange and raising of productivity potential. India's annual drainage in foreign exchange in the field of minerals, ores, metals and alloys is of the order of several hundred crores of rupees. This calls for immediate remedial measures including stepping up of mineral production, their export consistent with the principles of conservation and national economy, development of substitute processes and families of alloys and above all indigenous technical 'know-how' to find full scope and applications in our industries with Indian raw materials, skill and talent.

Desperate and yet chronic shortages of primary metals also call for steps to utilise drosses and related residues from metallurgical wastes, such as zinc dross for galvanising shops, aluminium dross, brass dross, reclamation of lead and processing of electro-metallurgical residues and muds. The serious scarcity and inadequacy of resources of metals such as copper, zinc, nickel, tin, tungsten, molybdenum, cobalt, etc. has necessitated short-term and long-range research and development studies. Add to this the current emergency and the story is complete of awakening afresh on the subject of 'substitution' at all levels—a subject on which the National Metallurgical Laboratory has been waging a battle and has offered a lone metallurgical battle for almost a decade now.

Dissolution of Steel and Absorption of Hydrogen by Steel during Acid Pickling in Presence of Inhibitor Part II

J. Konar
N. G. Banerjee

The paper presents the observations made on the effect of addition of inhibitors such as soluble starch, dextrin, potassium iodide, and diethylaniline and thiourea on the rate of dissolution and hydrogen pick-up by a plain carbon steel sample when pickled in sulphuric acid bath. Effects of the inhibitors on the steel having different carbon contents have also been compared.

Inhibitors diethylaniline and dextrin have been found satisfactory in inhibiting metal dissolution and hydrogen pick-up in all the three types of steel studied. Starch is found to be unsuitable in mild steel but acts most efficiently on medium and high carbon steel.

THE acid corrosion of metals is usually accompanied by the evolution of hydrogen. The hydrogen evolved in the atomic state during the acid-metal reaction can penetrate into metallic crystal lattice as interstitial atoms. Part of these diffused hydrogen atoms in the crystal lattice forms molecular hydrogen and remains lodged in the numerous microscopic pores (microcavities) in the matrix. Accumulation of molecular hydrogen in these microcavities is associated with high pressure which is the chief cause of formation of pickling blisters on the surface of the metals and other embrittlement effects perpetuated by hydrogen. It has been observed[1] that the amount of hydrogen produced at a metal surface during corrosion is not an important factor. The surface condition of a metal, which is affected markedly by inhibitors, is significant. Hydrogen pick-up is also influenced by the composition of the steel. I.N. Putilova et al[2] studied the rate of diffusion of hydrogen through steel having different carbon contents in a sulphuric acid medium. They observed that the hydrogen diffusion through the steel increases with the increase of carbon contents, is maximum at 0·7–0·8%C and again decreases when the carbon content reaches 1·2%. The study of problems associated with the diffusion of hydrogen into metals during pickling has gained importance during recent years.

Pickling brittleness has been found to diminish after a proper heat treatment of the pickled article.[3] Brittleness decreases even if the metal is left exposed to the atmosphere for a long period after pickling but the original ductility of the metal is not fully restored. Proper inhibition of hydrogen in the steel during pickling can eliminate the extra step between the pickling and finishing of the metals. Moreover, in industrial plating practice materials after pickling are quickly rinsed in running water and then immediately transferred to the plating bath to avoid any chance of surface oxidation.

The main object of the present investigation is to study the action of some common inhibitors on the amount of hydrogen picked up by the metal during pickling in the acid bath, and the effect of carbon contents in the steel on the mode of hydrogen pick-up during acid pickling.

The inhibitors studied are soluble starch, dextrin, potassium iodide, diethylaniline and thiourea. The inhibition action of the above inhibitors on the rate of dissolution is well known but their inhibition on the hydrogen pick-up has not yet been studied systematically. Organic inhibitors are considered to be better than inorganic inhibitors when the rate of dissolution is concerned and organic inhibitors selected for the study are commonly used in industry.

Halides were once supposed to accelerate acid attack,[4] but recently it has been observed that they are fairly good inhibitors.[5] And among the halides iodides are the best, so potassium iodide has also been selected for the present study.

Experimental procedure

In the present investigation the pickling bath consists of 7N sulphuric acid, chosen to get an accelerated pickling action in 4 hours time. Steel samples are cut from the normalised steel slab according to the size of $2·5 \times 1 \times 0·25$ cm. Their surface is freed of scales to maintain a uniform reaction rate during pickling. After pickling for 4 hours the sample is washed, dried at room temperature and the hydrogen is estimated then and there by the modified vacuum heating method. The procedure with an arrangement for measuring the hydrogen in the pickled sample has been described in a previous paper[6] from this Laboratory. The steel samples studied are mild steel (0·15%C, 0·76% Mn), and medium carbon steel (0·65% C, 0·90% Mn), and high carbon steel (1·1% C, 0·72% Mn). The rate of dissolution and hydrogen pickup for steels of different carbon contents using different inhibitors are graphically represented. The criteria of an ideal inhibitor are that the rate of dissolution should be low and at the same time the hydrogen pick-up in c.c. per dm^2 should also be low. So, for the comparative study the ratio of

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Messrs J. Konar, Senior Scientific Assistant and N. G. Banerjee, Scientist, National Metallurgical Laboratory, Jamshedpur.

hydrogen pick-up to metal dissolution H/d has been considered and the lower the ratio H/d the better is the performance of the inhibitor as is shown in Tables I, II and III.

TABLE I H/d ratio (mild steel) at different inhibitor concentrations

Inhibitor	Ratio at ·025% inhibitor	Ratio at ·05% inhibitor	Ratio at ·1% inhibitor	Ratio at ·2% inhibitor
Starch	1·64	1·53	1·09	1·42
Dextrin	0·64	0·56	0·56	0·74
Potassium iodide	0·35	0·38	0·42	0·73
Diethylaniline	0·30	0·28	0·30	0·96
Thiourea	0·79	0·75	0·84	1·04

TABLE II H/d ratio (medium carbon steel) at different inhibitor concentrations

	Ratio			
Inhibitor	·02% inhibitor	·05% inhibitor	·1% inhibitor	·2% inhibitor
Starch	1·40	1·34	1·38	1·42
Dextrin	1·87	2·63	2·24	1·54
Potassium iodide	6·03	10·35	13·41	25·03
Diethylaniline	2·33	2·21	1·87	2·02
Thiourea	6·56	11·84	18·37	16·06

TABLE III H/d ratio (high carbon steel) at different inhibitor concentrations

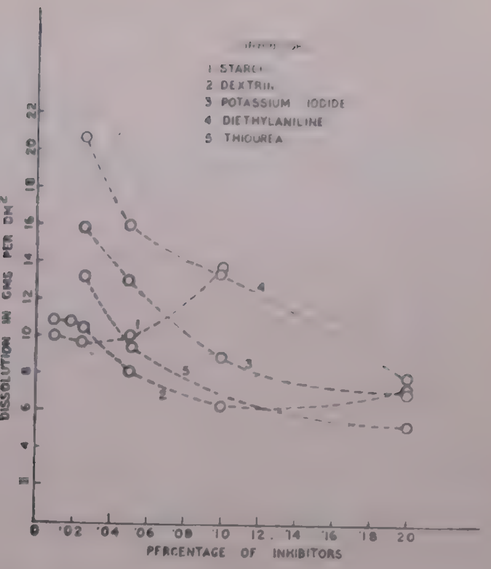
	Ratio			
Inhibitor	·02% inhibitor	·05% inhibitor	·1% inhibitor	·2% inhibitor
Starch	1·28	1·38	1·07	1·05
Dextrin	2·02	1·49	1·27	1·12
Potassium iodide	4·30	15·01	26·02	56·30
Diethylaniline	1·41	1·56	1·43	1·37
Thiourea	41·1	25·1	20·6	27·5

Discussion

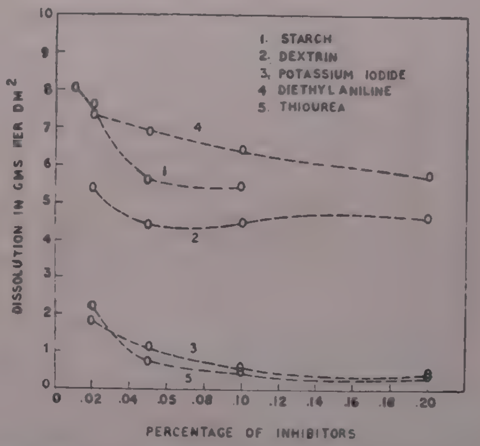
Starch reveals a peculiar behaviour both in inhibiting dissolution as well as in retarding hydrogen penetration in the steel. It inhibits the dissolution of medium and high carbon steels and promotes that of mild steel (Figs. 1, 2 and 3). It can neither inhibit the metal dissolution nor can it prevent hydrogen pick-up in mild steel during pickling. The rate of dissolution increases with the increase of the concentration of inhibitors. But it acts very efficiently in inhibiting metal dissolution and keeping the H/d ratio very low, in the case of medium carbon steel and high carbon steel. In the case of medium carbon and high carbon steel starch shows a better performance than dextrin and diethylaniline (Tables I, II and III).

Dextrin as an inhibitor acts efficiently in inhibiting metal dissolution and keeping the H/d ratio very low when mild steel is pickled, Dextrin shows a higher H/d ratio when acted on medium carbon steel and high carbon steel.

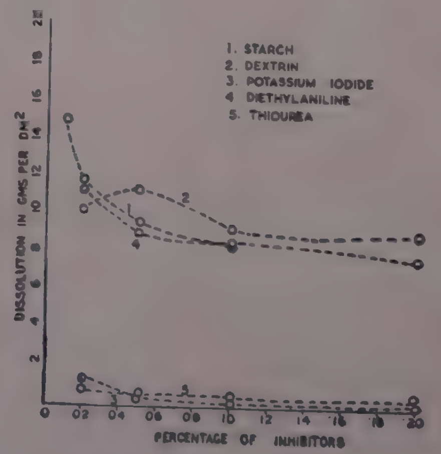
It has been found that potassium iodide is a mild inhibitor for mild steel when dissolution of metal is considered. It is responsible also for keeping the H/d ratio, which increases when the concentration of inhibitor increases, moderately low. Potassium iodide is useless for medium carbon and high carbon steel. The metal dissolution is practically nil (Figs. 2 and 3) and the H/d ratio is abnormally high. For medium carbon steel it is 6 to 25 and for high carbon steel it is 4 to 56 depending on the concentration of the inhibitor.



1 *Rate of dissolution of mild steel at different inhibitor concentrations*

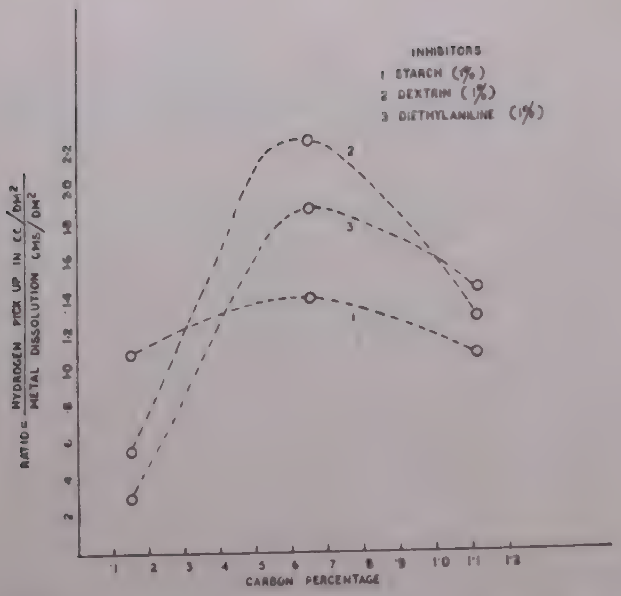


2 *Rate of dissolution of medium carbon steel at different inhibitor concentrations*



3 *Rate of dissolution of high carbon steel at different inhibitor concentrations*

Diethylaniline acts as a moderately better inhibitor in lowering dissolution with an increase of inhibitor concentration. Its action on mild steel is better than that on medium and high carbon steel when the H/d ratio is considered, as is evident from the tables. It works excellently well on mild steel. The ratio remains at a very low level in mild steel but in the case of medium carbon and high carbon steel the ratios are comparatively high (Tables I, II and III).



4 *Rate of diffusion in steel of different carbon contents*

The behaviour of the inhibitor thiourea in inhibiting the dissolution of metals is similar to that of potassium iodide. Dissolution is practically nil with medium carbon and high carbon steel. The ratio of hydrogen pick-up to metal dissolution for the mild steel is high and it increases with the increase in inhibitor concentration. The ratio is still higher in the case of medium carbon and high carbon steel (Figs. 2 and 3). For medium carbon steel the H/d ratio is 6–18 and for high carbon steel it is 20–41.

The influence of carbon content on the diffusion of hydrogen during dissolution of steel in the presence of starch, diethylaniline and dextrin has been represented in Fig. 4. It has been observed that the H/d ratio is maximum for medium carbon steel. This shows that hydrogen pick-up is more when the carbon content is nearly 0·65% and low in the case of mild steel and high carbon steel which is in agreement with Putilova's observation.[2]

Conclusion

It is of interest to note that some inhibitors act well for mild steel in inhibiting hydrogen pick-up and some are more effective in the case of high carbon steel. Starch behaves as a negative inhibitor in the case of mild steel but shows the best performance when tried in medium and high carbon steels; it keeps the H/d ratio lowest in both medium and high carbon steel. From the above study it has been observed that for medium and high carbon steels, starch is the most suitable inhibitor. Diethylaniline shows a lower ratio of hydrogen pick-up to metal dissolution in all the three types of steel, but remarkably for mild steel. So diethylaniline may be regarded as a useful inhibitor for all the steels. Dextrin also shows moderate performance for all types of steel. Potassium iodide and thiourea are useless for medium and high carbon steel for their abnormally high H/d ratio, but potassium iodide has got moderate inhibitive action on mild steel where H/d ratio has got a low value.

Acknowledgement

The authors wish to thank Dr B. R. Nijhawan, Director, National Metallurgical Laboratory, for his keen interest and permission to publish this paper. The authors are also thankful to Dr T. Banerjee, Dr B. C. Kar and Mr H. K. Chakravarti for their helpful suggestions.

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Measurement of Curie Temperature by An Induction Method

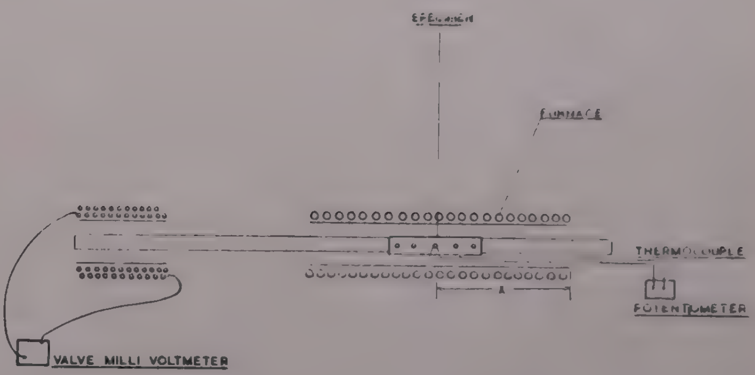
A. N. Sinha
L. J. Balasundaram

An induction method to measure the curie temperature of ferromagnetic materials is described. In this method the specimen whose curie temperature is to be measured is made the core of a circuit, the primary of which also acts as a furnace. The current induced in the secondary through the specimen is recorded by a millivoltmeter. Raising the temperature of the specimen by passing current through the primary results in loss of ferromagnetism of the sample and at the curie temperature due to complete and rapid loss of ferromagnetism a sudden reduction in induced e.m.f. is produced. The temperature at which a sudden reduction is seen from deflection in millivoltmeter is taken to be the curie temperature. The method has been standardised with armco iron and super spec pure nickel and the accuracy of determination is ±3°C.

THE curie temperature of ferromagnetic metals is the temperature at which ferromagnetism is lost with rise in temperature and has been measured by various methods, among which Sucksmith's magnetic balance,[1] and Weiss and Forrer method[2] are based on the measurement of magnetic properties. Other methods involve a change in property like electrical resistivity, thermo e.m.f. of the ferromagnetic specimen upon destruction of ferromagnetism. In the present method, the loss of susceptibility at the curie temperature is made use of.

In a circuit with a ferromagnetic material forming a core, the amount of induced e.m.f. in the secondary coil for a constant current in the primary depends upon the ferromagnetism of the sample and at the curie temperature of the core material there will be a change in the induced e.m.f. of the secondary coil due to destruction of the ferromagnetism of the core. In the present method, the material whose curie temperature is to be determined is made the core of the circuit and the temperature at which a sudden reduction in induced e.m.f. in the secondary is noted is taken to be the curie temperature.

The experimental arrangement is shown shematically in Fig. 1. The specimen whose curie temperature is to be measured is in the form of a rod 6″ long ½″ dia. and welded on both sides to mild steel (as in the present case, the specimen happens to have curie temperature less than mild steel) rods of ½″ dia. and 15″ and 7″ length and introduced into a furnace so that the specimen is in the uniform temperature zone of the furnace. The furnace also acts as the primary. One end of the composite rod is introduced into a tube over which a coil is wound and this acts as the secondary. The secondary terminals are connected to valve millivoltmeter.



1.

At room temperature, there is no current in the furnace, i.e. the primary. A small a.c. voltage is fed into the coil of the primary (i.e. the furnace) through a variac, and this voltage (i) induces current in the secondary, and (ii) raises the temperature of the specimen. Whilst the first effect is instantaneous, there is a time lag for effect (ii) and time is allowed for the specimen to attain the constant temperature. The induced e.m.f. of the secondary for a particular voltage of the primary, is recorded after the specimen has attained the constant temperature for that particular voltage of the primary. The input voltage is increased in small steps taking care each time for the furnace to attain the steady temperature and the corresponding induced e.m.f. in the secondary is noted. The induced e.m.f. in the secondary will be proportional to the current in the primary, with the specimen remaining ferromagnetic. With rise in temperature the ferromagnetism of the specimen is lost at first slowly and then rapidly and vanishes at the curie point. When the ferromagnetism of the specimen vanishes, it will be in a thin section of the sample at the centre of the furnace which attains the curie temperature earlier than the remaining sections. This thin section which has lost ferromagnetism is unable to convey the magnetic lines of force in portion X, to the secondary and hence there is a reduction in the induced e.m.f. which is shown by a sudden reduction in the valve millivolt meter. A graph of induced e.m.f. vs temperature of the

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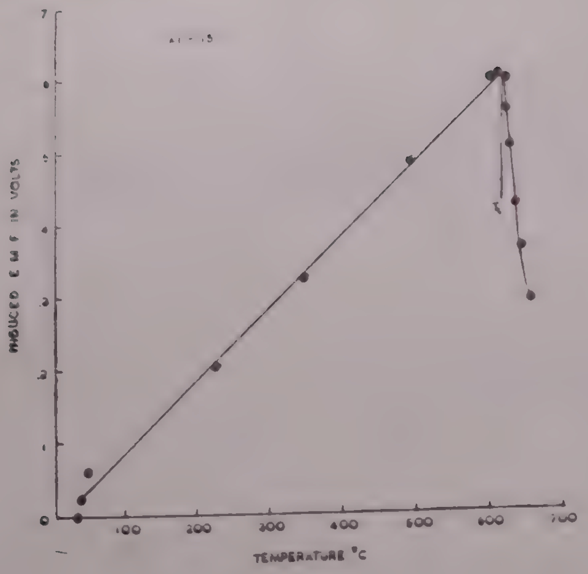

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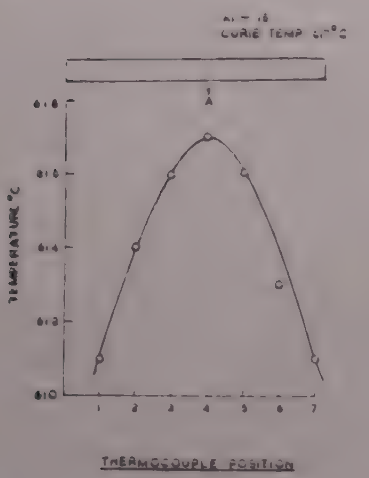

3.

specimen is shown in Fig. 2. and T_c is the temperature at which there is a sudden reduction in induced e.m.f.

The accuracy of the method depends upon the precision with which the temperature of the section of the specimen which first loses ferromagnetism is measured. For this a series of 5–7 holes are drilled in the specimen one centimetre apart and the curie temperature is measured with thermocouple in each hole keeping the specimen in the same position with respect to the furnace. A plot of the curie temperature vs the position of the thermocouple in the specimen, is shown in Fig. 3. The curie temperature is symmetrical about the hole which loses ferromagnetism first i.e. section A which is the first section to lose ferromagnetism as it attains the curie temperature earlier than sections on either side and hence it records the correct curie temperature. For the same reason the thermocouple in position one will record a lesser temperature than section 'A' as section 'A' loses ferromagnetism earlier than the section containing position one.

For each specimen Figs. 2 and 3 are plotted and the maximum temperature shown in Fig. 3 is taken as the correct curie temperature. The method has been standardised with armco iron and spec-pure nickel rod and the results are accurate to ±3°C.

Acknowledment

The authors wish to thank Dr B. R. Nijhawan, Director, National Metallurgical Laboratory and Dr Rajendra Kumar for their interest.

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Electrolytic Recovery of Tin from Tinplate Scrap

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In this investigation, attempts have been made to recover the metallic tin by electrolytic detinning of tinplate scrap. The electrolysis is carried out with a caustic soda bath. Stainless steel sheets have been used as cathode and the tinplate scrap, packed in the form of rectangular bundles, serves the purpose of the anode.

Experiments have been carried out to determine the optimum condition of concentration of caustic soda. sodium acetate, sodium stannate and sodium carbonate in the electrolyte, temperature of the bath, current density, amount of scraps to be charged, time of detinning and other factors such as dissolution and deposition of tin by electrolysis.

Due to repeated use of the same electrolyte, sodium stannate and sodium carbonate build up in the alkaline electrolyte, the latter due to absorption of atmospheric carbon dioxide. Fall in cathode C. E. is accompanied with it. Treatment with lime to remove carbonate restores the high value of cathode C. E. even though stannate contents remain high.

Recovery of metallic tin as cathode deposit has been up to 96·0% under a current density of about 13·5 amp/sq.ft with a current efficiency of 70·8%, the purity of the deposited metal being 99·8%. The maximum percentage of tin left in the detinned scrap has been 2·5% of the total amount of tin in the coating.

DETINNING is the term used in industry for the recovery of tin from tin containing wastes and scraps. In the case of scraps arising from tinplate manufacture, this will relate also to the reclamation of the base steel, after removing the tin coating.

Tinplate, which is the basic raw materal for containers and can manufacturing industry, is mild steel sheet commonly about 0·01″ thick, with coatings of tin averaging between 1 and 1·6% of its weight.

The scrap tinplate is not suitable for use in steelmaking when accompanied with such a large amount of tin. This amount will impair the physical and mechanical properties of finished steel by alloying with the product during the melting process. It is essential therefore that the tin be removed from the steel sheet before the latter has any value as scrap in steelmaking. Besides, the recovered tin in the form of secondary metal has got as much importance and industrial value as the virgin metal. USA,[1] which is the largest single user of tin in the world (US production of tinplate, solder and other alloys of tin is 68% to 75% of the total world production in the post-war period), is also the largest producer of secondary tin. She has to depend solely on import of ores and concentrates for her requirement of tin metal and the production of secondary metal from the scrap helps in adding to the imported supply.

This condition applies to India also. India has to import all her requirements of tin metal from abroad. But the recovery of secondary tin is not done in an organised manner though there is sufficient scrap tinplate available for this purpose.

Tin is a scarce metal and at the same time the most indispensable of all the base metals. Under the conditions, the urgency and importance of recovery of tin from tin containing wastes and scraps are too obvious to need emphasis.

Production of tinplate in India[2]

At present the Tinplate Company of India produces about 70 000 tons of hot dipped tinplate per annum. They are planning to double their cold reduction capacity and installation of up to 100 000 tons per annum of electrolytic tinplate capacity in addition to the existing facilities. The resulting total capacity is scheduled to be around 170 000 tons.

The Rourkela Works (Hindustan Steel Ltd) are installing six hot dipping lines of 10 000 tons capacity each. When these lines are installed the turning capacity of the Rourkela plant will be 60 000 tons annually. In addition there is provision for electrolytic lines of 120 000 tons annual capacity also.

At present the home consumption is nearly 150 000 tons of tin plate per year. The shortfall is made up by import.

Availability of scrap

During manufacture, about 1—1·5% of the total production of tinplate goes out as scrap in the shape of side clippings, defective plates, etc. About 10—15% of the tinplate used for manufacture of tin cans, metal boxes, etc. runs into scrap as trimmings and clippings. Besides, old tin cans and containers can also be regarded as suitable waste materials for recovery of tin. On the basis of the above considerations, the amount of scrap that may be available in India for recovery of tin is far above 20 000 tons per annum accounting for more than 200 tons of metallic tin per annum.

Recovery processes

Before the last world war, most of the tin was recovered as stannic chloride.[3] This compound was used quite extensively in the silk industry. With the sharp decline in the supply of silk during and after the war, there was an immediate increase in the production and consumption of secondary tin as the

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final form of recovered tin and currently about 85–90% of the recovery is being marketed as metal.

Processes for recovery of tin in metallic form from scrap tin plates consist essentially of the following steps :

(a) Cleaning the scrap in dilute caustic soda solution.
(b) Dissolution of the contained tin coat in a stronger solution of caustic soda with some oxidising agent, viz. sodium nitrate, sodium nitrite, air, etc. and formation of sodium stannate.
(c) Recovery of metallic tin from sodium stannate, with or without crystallisation and purification of sodium stannate.

Variation or elimination of one or more of the steps and addition of some minor treatment to the above general process form the major part of the subject matter of the large number of patents and processes worked on a commercial scale.

Among the more recent processes the one patented by Wakae Hosoda and Masao Mukai[4] specifies an aqueous solution of 300–500 gm of caustic soda with 50–150 gm of sodium nitrate per litre at 105–125°C for dissolution of tin from scrap. According to the process patented by Jean Marie Gustave Creusot[5] the tinplate scrap is compressed into briquette form and sprayed with a caustic soda solution containing lead oxide or sodium nitrate. Additional oxidising action is derived from the air streaming through the vacant spaces in the briquettes.

The recovery of tin from the solution is usually done by electrolysis. There are, nevertheless, some processes in which tin is recovered by chemical reduction. A.J. Krombholz[6] describes a method in which the separated sodium stannate is treated with sulphuric acid to obtain tin hydroxide which is reduced with anthracite coal at 2 200°F to obtain 99·94% tin. B. Chatterjee[7] describes a method where tin is removed from scrap as tin chloride by treatment with dry chlorine. Tin chloride is next treated with a more electropositive metal, for instance zinc, when tin precipitates out as a powder. This powder can be melted into lumps.

It may be noted that during electrolytic deposition of metallic tin, the evolved oxygen usually goes to waste. There have been some attempts to utilize this oxygen for dissolution of tin. Frederick A. Lowenheim's[8] patent describes a process in which the anodically evolved oxygen is utilized for dissolution and oxidation of tin to stannate radical. The metal is recovered by electrolysis directly from the bath containing dissolved stannate.

The latter method has several attractive features. In the first place, it utilizes anodically evolved oxygen for dissolution of tin and thus effects economy in chemicals. Secondly, it by-passes the stage involving crystallisation, purification and redissolution of sodium stannate, prior to recovery of tin from it. This makes all the equipment relating to this stage unnecessary. Under Indian conditions such simplification in method and equipment is desirable and it is therefore worthwhile to examine the method for commercial application. A programme of experiments was therefore worked out to carry on the investigation.

Experimental procedure

The process adopted at the National Metallurgical Laboratory for trial essentially consisted of the following steps :

(1) Compaction of the waste tin plates.
(2) Pretreatment for removal of organic coatings, if any.
(3) Treatment of the compacted and treated tin-plate waste in a non-diaphragm electrolytic cell as anode with caustic soda solution and simultaneous recovery of tin as cathode deposit.
(4) Melting of cathodically recovered tin and casting it into buttons
(5) Washing the detinned scrap bundles free from caustic soda for ultimate utilization in the steel melting furnace.

The scrap was compacted manually in bundles measuring 4″×3″×1″ and weighing about 250–300 gm. These bundles were rinsed with a solution containing 10 gm of caustic soda per litre at 25–30°C. The electrolytic cell consisted of a 3-litre glass beaker containing 2·5 litres of electrolyte. Polished and cleaned stainless steel sheets measuring 5″×3″×1/16″ were used as cathodes. Experiments were carried out to find out the influences of concentration of caustic soda, sodium stannate, sodium acetate, sodium carbonate, current density, temperature and a few other factors on dissolution and deposition of tin by electrolysis.

Experimental data

TABLE : I Effect of concentration of caustic soda (C.P.)

Temp. of electrolytic bath		60°C
Cathode C.D.	...	13 A/sq. ft
Current	...	5 amp.
Voltage	...	2·0–2·5
Wt. of scrap tinplate (anode)	...	250 gm
Time of eleetrolysis	...	60 minutes
Conc. of sodium acetate fixed at	...	5 gm/litre

Bxpt. No	Concentration of NaOH. gm/litre	% C. E. at cathode	State of detinning
1	40	33·0	Detinning incomplete. There was a tendency toward rapid rise of temperature and the cell voltage was unsteady.
2	50	38·0	
3	60	44·6	
4	65	45·1	
5	70	48·5	
6	75	48·6	
7	80	48·0	
8	90	The deposits of tin started floating on the electrolyte.	

TABLE II : Effect of the concentration of sodium acetate in electrolyte.

Concn. of NaOH in electrolyte was kept at 70 gm/L. Temperature, current density, voltage, amount of tinplate scrap treated, time of electrolysis, etc. as in Table I

Expt. No.	Concentration of sodium acetate. gm/litre	% C, E, at cathode	State of detinning
1	5·0	50·0	Detinning 60–80%
2	6·0	54·8	
3	7·0	53·9	
4	8·0	59·0	
5	9·0	59·8	
6	10·0	59·8	

TABLE III : Variation of C E when spent electrolyte is recycled without regeneration. Carbonate content is not estimated.

Sodium acetate (concn.)—8 gm/L
Other conditions as in Table II

No. of cycles	Sod. stannate (concn.) gm/L	% C. E. at cathode	State of detinning
1st	nil	60·0	about 80%
2nd	1·9	58·0	70%
3rd	3·2	56·2	67%
4th	5·3	44·0	Incomplete
5th	7·1	39·0	,,
6th	10·3	36·7	,,
7th	14·3	33·0	,,

For removal of carbon dioxide from the above recycled electrolyte, a slight excess of freshly slaked lime was added when carbon dioxide present as sodium carbonate precipitated out as insoluble calcium carbonate. The excess of lime and calcium carbonate were filtered out before using the electrolyte for electrolysis. This process has regenerated the electrolyte and in spite of the high sodium stannate content after the seventh cycle the current efficiency obtained is quite satisfactory as shown in Table IV.

TABLE IV : Variation of current efficiency in regenerated electrolyte after the 7th cynle when carbonate is removed with lime treatment.

Concentratlon of carbon dioxide as sodium carbonate in the regenerated electrolyte less than 0·05 gm/L

Concn. of sodium stannate-about 14 gm/L.
Other conditions same as in Table II.

Expt. No.	C. D. at cathode	T°C	Cell voltage	% C. E. at cathode	% detinning
1	13·0	60	2·1	70·8	96·3
2	13·4	60	2·1	71·8	96·5

TABLE V : Effect of C. D. at cathode on deposition and dissolution of tin.

Concn. of caustic soda	70 gm/L	in fresh electrolyte
,, sodium acetate	8 gm/L	
Temperature	70°C	
Time	60 minutes	

Expt. No.	C. D. on cathode A/ft²	Wt. of deposit gm	% C. E. at cathode	Wt. of scrap at anode gm	% recovery of tin as metal	% detinning
1	6·00	0·65	26·1	196	low	Incomplete
2	6·65	1·60	58·0	194	56·0	70·0
3	13·30	3·20	60·0	260	77·0	90·0
4	13·30	3·66	66·1	232	94·8	96·3
5	13·50	4·66	70·8	300	97·0	98·0
6	14·10	3·41	63·5	262	81·4	93·0
7	19·90	3·25	56·0	251	80·1	90·0

TABLE VI : Effect of temperature on detinning.
Other conditions as in Table V.

Expt. No.	Temp. °C	Voltage (volts)	Nature of deposit	Detinning	Remarks
1	50	1·5	Spongy deposit low C.E.	Incomplete	
2	60	2·0	Spongy deposit	Satisfactory and above 95%	Cathode C.E. above 70%. No appreciable change in amount of deposit and detinning
3	70	2·5	,,	,,	
4	75	3·2	,,	,,	

Optimum conditions for electrolysis

It will be found from Tables I, II. V and VI that the optimum conditions for detinning and deposition of tin may be taken as follows :

Conc. of caustic soda in electrolyte	70 gm/L
,, sodium acetate ,,	8 gm/L
Current density on cathode	13·5 A/sq ft
Temp. of electrolysis	60°C

Results obtained in an experiment carried out under the above conditions are given in Table VII.

TABLE VII

Anode—300 gm of tinplate scrap, pressed into one bundle measuring 4″×3″×1″ ; containing 4·83 gm of tin

Cathode—Two stainless steel plates, measuring 5″×3″×1/16″ each
Time of electrolysis—One hour at 5·1 amp×2·1 volts

Data

(a) Amount of tin recovered at cathode	4·66 gm	
(b) Amount of tin left undissolved	0·12 gm	
(c) Amount of tin left in the electrolyte	0·05 gm	(by
(d) Purity of cathode deposit	99·8%	difference)
(e) C. E. at cathode	70·8%	

(f) % tin recovery as metal $\frac{4\cdot66}{4\cdot83}\times100=96\cdot4\%$

(g) % tin locked up as stannate $\frac{0\cdot05}{4\cdot83}\times100=1\cdot0\%$

(h) % tin left in detinned scrap $\frac{0\cdot12}{4\cdot83}\times100=2\cdot5\%$

(of total amount of tin in the coating)

Discussion

1. Table III shows the effect of using the same electrolyte repeatedly for fresh detinning and deposition of tin. Concentration of stannate increases in the aged electrolyte and so does its carbonate content which has not been shown in the table. C.E. at cathode falls with aging.

Table IV shows that treatment with lime to remove carbonate restores the high value of cathodic C. E. even though stannate content remains high. The low value of C.E. while using aged electrolyte is therefore ascribed to its carbonate content.

2. An approximate idea about the cost of power involved in the process may be useful.

From Table VII, for deposition of one kilogram of tin power (D.C.) required is as follows :

$$\frac{5\times 2{\cdot}1\times 1\,000}{4{\cdot}66\times 1\,000}\ \text{kWh}=2{\cdot}25\ \text{kWh}$$

$\therefore$ Cost of power (D.C.) for one kg of tin $=2{\cdot}25\times 6$ paise $+6$ paise per unit $=13{\cdot}6=14$ paise approximately.

For production of one tonne of tin

Cost of power (D.C. only, at 6 paise per kWh)	Rs 140·00
Cost of scrap (72 tonnes at Rs 130 per tonne)	Rs 9 160·00
	Rs 9 300·00

To this, costs on account of chemicals, labour, fixed charges. overheads, etc. will have to be added. Estimates of these cost items can be done with data from experiments on a pilot plant scale. Nevertheless, considering that the market price for tin is Rs 15 000 per tonne and the detinned scrap has a potential market, profitable recovery of tin from scrap may be expected.

The prospect of electrolytic recovery of tin is bright and the extent of profitability of such recovery on a large scale in India may be examined by preparing a project report.

Acknowledgements

The authors acknowledge with gratitude the helpful suggestions given by Dr T. Banerjee, Scientist and Dr B. C. Kar, Scientist, during the course of this work and thank Dr B. R. Nijhawan, Director, National Metallurgical Laboratory for his keen. interest in the work.

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Thermal Beneficiation of Low Grade Chrome Ore from Vagda Deposits, Ratnagiri District, Maharashtra

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A low grade chrome ore from Vagda deposits, Ratnagiri dist., Maharastra. which could not be upgraded to the desired Cr : Fe ratio, by conventional physical methods of beneficiation, was successfully beneficiated to yield a metallurgical grade by preferential roast reduction and acid leaching. A table concentrate of the ore containing 44·93% Cr_2O_3, 15·39% total iron, 14·9% Al_2O_3, 8·9% MgO, 2·3% SiO_2, 1·1% CaO and an initial Cr : Fe ratio of 1·53 : 1 was reduced with varying quantities of solid reducing agent, at different temperatures and iron leached with dilute sulphuric acid. The Cr : Fe ratio thereby increased to 8 : 1 with more than 87% chromium recovery by preferential reduction of—72 mesh (B.S.S,) size ore with the—170 mesh (B.S.S.) size coke, at 1 250°C for a period of 2½ hours and subsequent leaching with dilute sulphuric acid. It has heen observed that chromium dissolution can be suppressed appreciably by controlled leaching with restricted amount of sulphuric acid, to yield a metallurgically suitable beneficiated chrome ore.

INDIA possesses fair reserves of low grade chrome ores with chromium : iron ratios less than 3 : 1, which cannot be directly utilized for production of standard grade ferro-chrome. These ores are generally not amenable to conventional methods of ore beneficiation, since chromium and iron are held chemically in the chrome spinel. Separation of chromium and iron can, however, be effected by a chemical attack on the spinel. The usual chemical methods for separation of chromium and iron are based on the use of alkalies, acids or chlorination. Alkali processes give rise to chromates or dichromates which can be blended with the untreated ore either as such or after reduction to chromium sesquioxide. The blended ore thus obtained can be utilized for metallurgical purposes in view of the improved Cr : Fe ratio. The acid process comprising of leaching with sulphuric acid either may give a basic sulphate which can be roasted to Cr_2O_3 or it can yield chromic acid by electrolytic oxidation of the leach liquor. Differential chlorination at elevated temperatures for separation of iron and chromium has also been reported.[1–4] Selective chlorination is, however, difficult and the separation can only be achieved by fractional condensation of the volatile chloride.

Thermal methods of beneficiation of low grade chrome ores include selective reduction of iron in solid or liquid state. Alteration of the ore requires very high temperature and is carried out by melting the ore with a suitable flux. The altered ore is then subjected to physical methods of beneficiation for separation of ferrous gangue material. Smelting of the low grade ore with coke leads to reduction of most of the iron yielding thereby a chromium rich slag and a chromium containing pig iron. The slag can be used as a starting material for production of ferro-chrome. Greater selectivity in reduction of iron can be achieved by carrying out the reduction in solid state at a comparatively lower temperature. Thermodynamic data[5] have shown that for pure chromite, the selective reduction of the iron oxide part can be carried out with coke at a temperature below 1 230°C. A systematic investigation conducted earlier on the selective reduction of iron in solid state using gaseous[6] as well as solid carbonaceous reducing agents[5] has resulted in evaluating a general method for beneficiation of the low grade chrome ores. The method consists in preferential reduction of the iron oxide constituent of the ore by carbonaceous reducing agents and removal of the reduced iron by subsequent acid leaching. Low grade chrome ores from various parts of the country have been investigated at National Metallurgical Laboratory for their suitability to respond to the above method of beneficiation and this work forms a part of such investigations.

The ore sample

A sample of low grade chrome ore from the Vagda deposits of Ratnagiri district, Maharastra, was received from the Director, Geological Survey of India, for beneficiation studies. The ore, as received, analysed 33·14% Cr_2O_3, 21·51% FeO, 14·5% MgO, 14·74% SiO_2, 11·0% Al_2O_3, 2·24% CaO and 2·13% loss on ignition at 950°C. Microscopic examination[7] of the ore indicated the presence of olivine as the principal gangue mineral followed by chlorite-serpentine group of minerals, talc, muscovite and traces of hypersthene. The only other minerals besides chromite were ilmenite and magnetite. Chromite occurred as hypidiomorphic grains and was disseminated in the gangue which was interstitial as well as in the form of inclusions inside the chromite grain. Chromite amounted to about 60% by weight in the composite sample. The size of chromite grains varied from 0·024 mm to 1·117 mm

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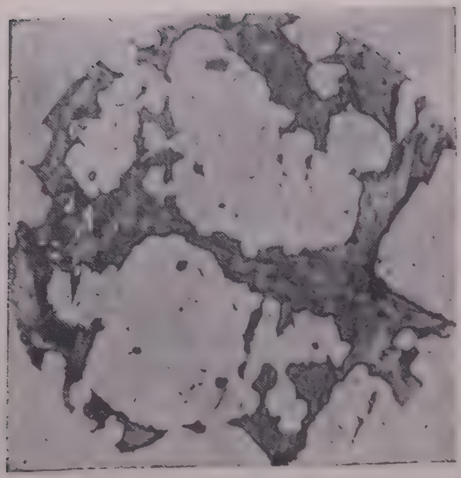
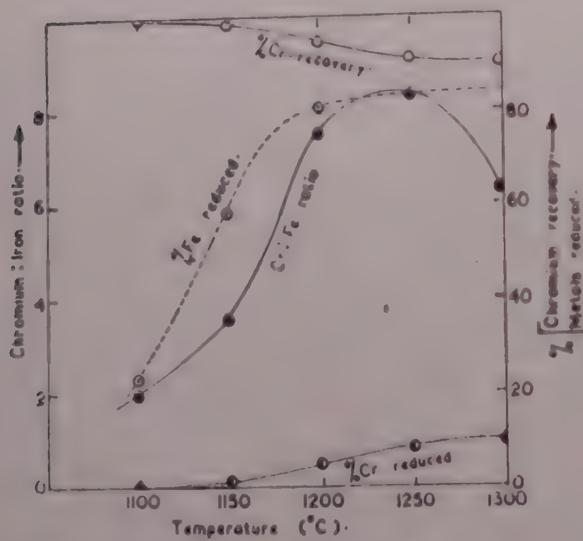


1 *Photomicrograph of Vagda chrome ore showing replacement of chromite by silicate gangue. Under reflected plane polarised light* ×112



2 *Effect of temperature on reduction*

with an average of 0·203 mm corresponding to −52 mesh (B.S.S.). The liberation of chromite was fairly good at about 52 mesh (B.S.S.) size. The petrographic examination of the ore sample indicated that the gangue minerals can only be removed by physical methods and no marked improvement effected in the Cr. : Fe ratio. A table concentrate[7] of the ore analysing 44·93% Cr_2O_3, 15·39% total iron, 14·9% Al_2O_3, 8·9% MgO, 2·3% SiO_2, 1·1% CaO and Cr : Fe ratio of 1·53 : 1 was used for thermal beneficiation studies. The concentrate was obtained at −72 mesh (B.S.S.) size with an average particle diameter of 0·120 mm (120m).

Procedure

Weighed amounts of chrome ore concentrate and coke were briquetted with 1% dextrine in the presence of 2% moisture under a pressure of 5 000 p.s.i. The coke sample used for the investigation contained 75·52% fixed carbon, 22·53% ash and 1·95% volatiles. The dried briquettes were placed in a tightly covered crucible and heated at a desired temperature for a specific period in a crucible furnace. The briquettes were cooled under cover after reduction and crushed to pass through 100 mesh (B.S.S.) sieve. Weighed amount of reduced ore powder was leached with an excess of 10% (by volume) sulphuric acid solution under boiling condition for an hour. The slurry was then filtered and the residue washed free from acid. The leach cake was air dried at 110°C. Cr : Fe ratio was calculated either from direct analysis of the leach cake.

Experimental results

Effect of temperature on reduction

A series of tests were carried out to find the effect of temperature within the range 1 100°C to 1 300°C on the reduction reaction. Briquettes containing −72 mesh (B.S.S.) ore and −170 mesh (B S.S.) coke with an ore : coke ratio of 1 : 0·074 were heated at a specific temperature for three hours.

The effect of temperature on the Cr : Fe ratio of the residue, chromium recovery as well as extent of the reduction with temperature are shown in Fig. 2.

It was observed that the percentage of iron reduced and dissolved on leaching sharply increases from 22·84 to 80·78 at 1 200°C and that no improvement in reduction of iron was noted on increasing the reaction temperature from 1 250° to 1 300°C. Chromium reduction gradually increased from 0·81% at 1 150°C to 9·74% at 1 300°C, and within the same temperature range the chromium recovery decreased from 99·19% to 90·26%. Concomitant with the extent of chromium and iron reduction, the Cr : Fe ratio of the beneficiated ore increased steeply from 1·97 to 8·41 with increase in temperature from 1 100°C to 1 250°C and decreased to 6·4 as the temperature was raised to 1 300°C. It is thus concluded that the maximum temperature during roast reduction should not exceed 1 250°C.

Particle size of reactions

A series of experiments were carried out at 1 250°C for 3 hours with 7·4 parts of −200 mesh (B.S.S.) size of coke per 100 parts of ore. The average particle size of the ore used was varied from 0·120 mm to 0·38 mm. The chromium recovery and the Cr : Fe ratio obtained by using varying size of ore is indicated in Table I.

No appreciable differences were observed either in Cr : Fe ratio or the chromium recovery, if the particle size of ore was reduced from 120 μ to 38 μ. The chromium : iron ratio averaged 8·3 with 91% chromium recovery. The concentrates can thus be directly reduced with coke without any further grinding.

In a further set of experiments, the ore size was kept constant at −72 mesh (B.S.S.) with an average particle diameter of 0·0836 mm and the size of coke was altered from −72 to −200 mesh (B.S.S). The reduction was carried out for three hours at 1 250°C. The chrome : iron ratio and the chromium recovery obtained by using varying size of coke are indicated in Table II.

TABLE I Effect of particle size of ore on reduction.

Temperature of reduction = 1 250°C.
Time of reduction = 3 hours.
Size of coke = −200 mesh (B.S.S.)

Sl. No.	Size of ore (B.S.S)	Average particle size (mm)	Cr/Fe ratio	% chromium recovery
1	−72 mesh	0·120	8·41	91·66
2	−100 ,,	0·0836	8·27	90·84
3	−120 ,,	0·07374	8·49	91·81
4	−170 ,,	0·0492	8·05	89·54
5	−200 ,,	0·038	8·40	90·90

TABLE II Effect of size of coke on reduntion.

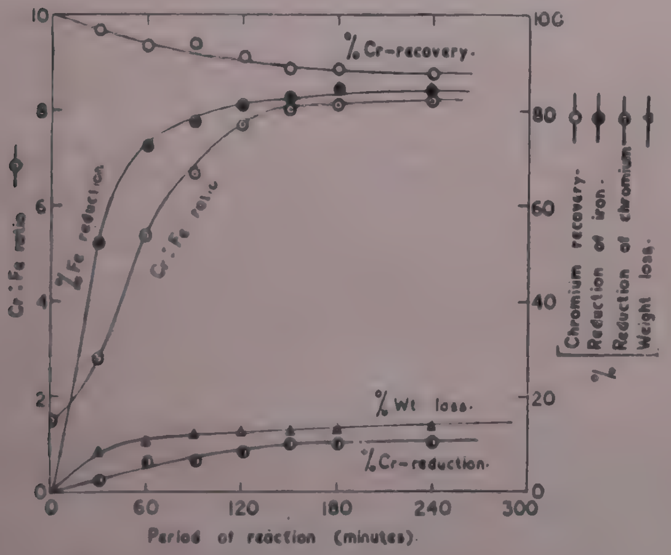
Size of ore = −72 mesh (B.S.S.)
Temperature of reduction = 1 250°C.
Time of reduction = 3 hours.

Sl. No.	Size of coke (B. S. S)	Average particle diameter (mm)	Cr/Fe ratio	% chromium recovery
1	−72 mesh	0·1084	6·11	95·01
2	−100 ,,	0·0786	6·91	94·14
3	−120 ,,	0·0746	6·61	94·32
4	−170 ,,	0·05657	7·29	93·78
5	−200 ,,	0·038	8·41	91·66

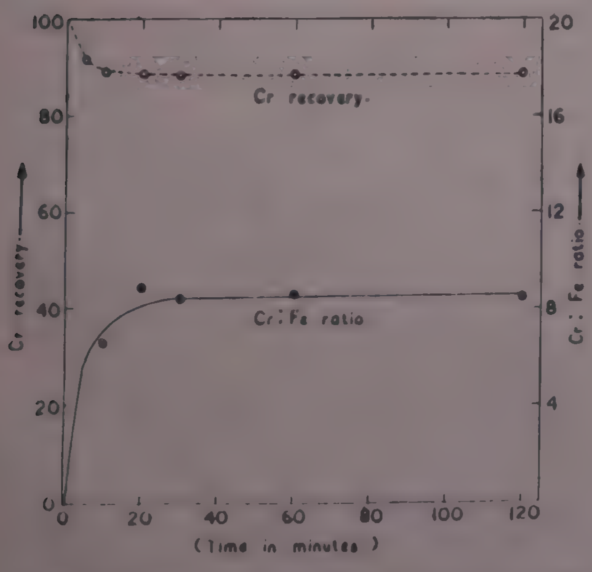
Using −72 mesh (B.S.S) coke, the Cr : Fe ratio and chromium recovery was 6·11 and 95·01% respectively. As the size of coke was decreased to −200 mesh (B.S.S) the Cr : Fe ratio increased gradually to 8·41, recording a fall in chromium recovery to 91·66%. A combined consideration with regard to Cr : Fe ratio and chromium recovery suggested the optimum coke size to be −170 mesh (B.S.S).

Kinetics of reduction

Briquettes were prepared with −100 mesh (B.S.S.) size of chrome ore concentrate and −170 mesh (B.S.S.) size of coke and were reduced at 1 250°C for different periods. The extent of reduction and the degree of beneficiation at different intervals are graphically represented in Fig. 3.



3 *Progress of reduction with time*



4 *Study of kinetics of leaching of Vagda chrome ore*

It was observed that the Cr : Fe ratio of the ore improved from 1·53 to 2·81 within the initial 30 minutes 5·4 after 60 minutes and thereafter steadily increased and Cr : Fe of 8·37 was obtained after 240 minutes of reduction. The gradual improvement in the Cr : Fe ratio with time was due to the faster reduction rates of iron oxides. It was also observed that iron oxide reduction was much faster than the reduction of chromium oxide ; 52·58% of iron was reduced within the first 30 minutes against the 2·7% chromium reduced. With a further increase in reduction period to 240 minutes whilst 84·07% of iron was reduced, chromium reduction was only 12·73%. The improvement of the Cr : Fe ratio of the ore is thus a direct consequence of the differential rates of reduction of oxides of iron and chromium due to which the Cr : Fe ratio increases.

Leaching characteristics

A sample of reduced chrome ore concentrate was obtained by reducing −100 mesh (B.S.S) ore concentrate with −100 mesh (B.S.S) coke at 1 250°C for a period of two and half hours. The reduced briquettes were crushed to −100 mesh (B.S.S) for leaching studies.

A stock solution of 10% (by volume) sulphuric acid was prepared and standardised titrimetrically. The strength of this acid corresponded to 177·3 gm H_2SO_4 per litre. The progress of leaching was studied under boiling conditions by continuing leaching of a weighed amount of reduced ore powder with the stock sulphuric acid for a specified period. The acid solution was pre-boiled and transferred in boiling condition to the reduced ore to mark the commencement of leaching. After the leaching had continued for a specific period the contents were chilled with ice and diluted with ice cold water followed by quick filtration under suction. The leach liquor analysis was used to calculate the degree of beneficiation. The results of these tests are graphically indicated in Fig. 4.

It was observed from Fig. 4 that leaching was practically completed within 30 minutes at boiling temperature. Some leaching experiments were carried out under boiling conditions with controlled additions of acid for leaching purpose. During these tests, the pulp density was kept unaltered by dilution. Earlier, it has been observed by the authors[5] that dilution has no appreciable effect on leaching and therefore it can be expected that in the present test it will not lead to any erratic conclusion by diluting acid to correct pulp density. The results are shown in Table III.

It appears conclusive from Table III that chromium dissolution can be suppressed by the use of a higher acid ratio. A high chromium recovery is obtained with

TABLE III Effect of amount of acid on leaching

Sl. No.	Acid* ratio	% soluble metal Fe	Cr	Cr/Fe ratio	% chromium recovery
1	10 : 9	69·40	4·41	4·77	95·59
2	1 : 1	70·17	5·16	4·85	94·84
3	9 : 10	74·23	6·76	5·52	93·24
4	1 : 10	84·01	11·06	8·48	88·94

$$* \text{ Acid ratio} = \frac{\text{Theoretical amount of acid required}}{\text{Actual amount of acid added}}$$

as high an acid ratio as 10 : 9, while the Cr : Fe ratio was 4·77, a value well above the specification for metallurgical grade ore.

Conclusions

A low grade chrome ore from Vagda deposit of Ratnagiri district, Maharastra, containing initially 33·14% Cr_2O_3, 21·51% FeO, 14·5% MgO. 14·74% SiO_2, 11·0% Al_2O_3 and 2·24% CaO could not be upgraded to meet specifications for metallurgical use by conventional ore-dressing method. A table concentrate of the ore containing 44·93% Cr_2O_3, 15·39% total iron, 14·9% Al_2O_3, 8·9% MgO, 2·3% SiO_2, 1·1% CaO and an initial Cr : Fe ratio of 1·53 : 1 was used for thermal beneficiation test comprising of preferential reduction of iron and its subsequent removal by acid leaching

It has been established that the chrome ore concentrate can be reduced at 1 250°C for a reaction period of two and half hours in briquetted form utilizing −72 mesh (B.S.S.) size of ore and −170 mesh (B.S.S.) size of coke. The reduced product can be crushed to −100 mesh (B.S.S.) size and leached with dilute sulphuric acid under boiling conditions. Leaching is practically complete within 30 minutes under boiling conditions. It is possible to suppress dissolution of reduced chromium by using restricted amount of acid for leaching. The table concentrate of the chrome ore could be upgraded to a Cr : Fe ratio

recovery under best reducing conditions and without any special control during the leaching procedure. A controlled leaching could raise the value for chromium recovery to higher than 95% to obtain a beneficiated chrome ore having a Cr : Fe ratio of about 4·8.

Acknowledgements

The authors wish to record their grateful thanks to Dr B. R. Nijhawan, Director, National Metallurgical Laboratory for his keen interest and helpful suggestion during the investigation report. Thanks are also due to Messrs D. V. Raman and M. S. Chopra for their help in chemical analysis and petrological examination.

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Apparent Activation Energy of Decarbonisation of Fe-C Melts

P. K. Sen

The effect of temperature on the rates of decarbonisation of Fe-C melts, subjected to two different oxidising gaseous media, viz., still air and a mixture of 92% argon and 8% oxygen has been studied. Experiments were carried out in a graphite resistance furnace in the temperature range 1 450°C–1 650°C. The effect of temperature on the rate of carbon oxidation is found to be considerable. Within the temperature range investigated, the net rate doubles itself for both the gaseous media. The apparent activation energies have been calculated to be 28·95 kcal. for argon-oxygen mixture and 31·02 kcal for still air atmosphere. The calculated values have been compared with those found by Vallet for open hearth melts and Watanabe et al for laboratory melts and the discrepancies are discussed. Analysis of laboratory data indicates the presence of a critical carbon concentration range.

CARBON oxidation reaction is one of the most important reactions in steelmaking. The gaseous product of reaction causes boiling of the bath, increases the contact between the reacting phases and stimulates the heat and mass transfer in the system. Hence the development of steelmaking processes is based on the correct approach to the knowledge of kinetics of this oxidation process. Though the reaction between dissolved carbon and oxygen can be represented by a simple stoichiometric equation, the overall process is in reality much more complicated, as it includes the stages of migration of the reacting substances in the heterogeneous gas-slag-metal system. The complexity is further enhanced by the surface active nature of both carbon and oxygen dissolved in molten iron.

The complex decarbonisation process, comprising of several interdependent physical and chemical steps, has attracted the attention of investigators over the last two decades. A host of investigators have attacked the kinetic problem from different points of view, indicating one or the other of the physical and chemical steps as the rate-controlling one, the details of which have been discussed elsewhere.[1] Perhaps the most generalised theory based on diffusion kinetics mechanism, has been proposed by Phillipov[2] incorporating the surface adsorption of both carbon and oxygen. According to Phillipov there exists a critical carbon concentration, above which the rate of carbon oxidation in the bath is dependent on the oxygen potential of the oxidising phase, the specific surface area and the rate constant of migration of oxygen to the reaction surface, but below which the rate of carbon oxidation will be dependent on carbon concentration of the bath, specific reaction area and the rate constant of migration of carbon to the reaction surface. Evidence of dependence of rate of carbon oxidation on carbon concentration of the bath at low concentrations has been found in industrial open hearth melts[3] as also in laboratory melts[2, 4] including the present investigation.

Experimental procedure

Melts were prepared in magnesite crucibles. The crucibles were made in the laboratory by a specially designed die. The dead burnt magnesite had the following sieve analysis :

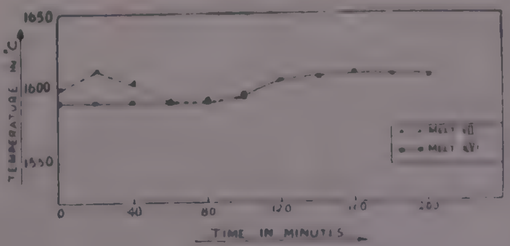
−10+20 B.S.S.	... −5·0%
−20+30 B.S.S.	... −5·0%
−30+40 B.S.S.	... −5·0%
−40 B.S.S.	... −85·0%

For every 100 gm of magnesite powder 8 ml of 1 : 10 sulphuric acid was used as binder. The crucibles were then prepared in the steel die. The crucibles were air dried at 220°C and subsequenly sintered at 1 550°C.

Two gaseous oxidising media were used. In the first series (Melts I–IV) still air and in the second (melts V–XIV) a mixture of 92% argon and 8% oxygen were used. The commercial purity argon was specially purified by passing through a tube packed with copper turnings kept at 700°C, then through a bubbler containing alkaline pyrogallol before mixing with oxygen. The flow rate of the mixture was kept at 1 litre per minute. Flowmeters for argon and oxygen were previously calibrated against a standard flowmeter.

Temperature measurements were done by an optical pyrometer which was previously calibrated against a standard thermocouple both for empty crucible and crucible with molten charge for the temperature ranges used for the experiment. Temperature curves for two typical melts (Nos. VIII and XVI) have been reproduced in Fig. 1.

Eighteen Fe-C melts were prepared and their oxidation behaviours were studied in three sets. The raw materials used in all the cases were Armco Iron sheets and pure graphite powder. In the first set four melts were prepared and their oxidation behaviours were studied at temperatures 1 500°C, 1 550°C, 1 600°C, and 1 650°C. For the second set the gaseous medium used was a mixture of 92% argon and 8% oxygen. Ten melts

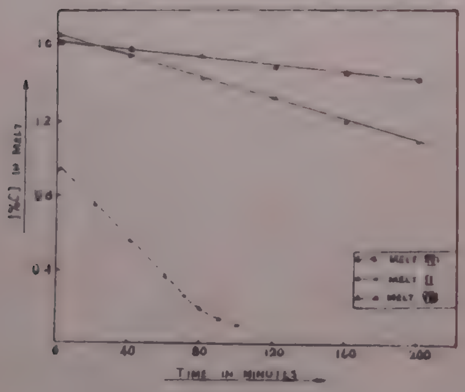


1 *Showing variation of temperature with time for two typical melts*

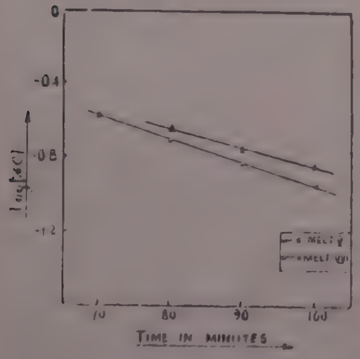
Mr P. K. Sen, Associate Professor in Metallurgical Engineering, Indian Institute of Technology, Kharagpur.

TABLE I Composition variation of different results with time

Melt No.	Temperature	Oxidising gas	Total flow rate	Minutes										
				0	20	40	60	80	100	120	140	160	180	200
I	1650°C	Still air	—	1·86	1·81	1·73	166	1·61	—	—	—	—	—	—
II	1600°C	,,	—	1·66	1·60	1·56	150	1·43	1·39	1·33	1·26	1·19	1·15	1·10
III	1550°C	,,	—	1·96	1·92	1·87	183	1·79	1·75	1·70	1·65	1·62	1·57	1·53
IV	1500°C	,,	—	1·58	1·55	1·50	147	1·44	1·40	1·37	1·33	1·29	1·25	1·22
				0	10	20	30	40	50	60	70	80	90	100
V	1650°C	92% Ar 8% O_2	1 lit/min	1·15	1·03	0·92	0·80	0·67	0·54	0·45	0·32	0·19	0·14	0·11
VI	,,	,,	,,	1·61	1·50	1·35	1·24	1·12	0·99	0·85	0·76	0·60	0·50	0·38
VII	1600°C	,,	,,	1·57	1·47	1·37	1·26	1·17	1·06	0·95	0·86	0·76	0·66	0·56
VIII	,,	,,	,,	0·95	0·86	0·75	0·65	0·56	0·46	0·37	0·26	0·22	0·17	0·14
IX	1550°C	,,	,,	1·53	1·45	1·36	1·29	1·20	1·11	1·03	0·97	0·88	0·79	0·71
X	,,	,,	,,	1·42	1·34	1·26	1·17	1·09	1·02	0·95	0·87	0·78	0·70	0·63
XI	1500°C	,,	,,	1·39	1·33	1·26	1·18	1·13	1·07	1·00	0·94	0·87	0·80	0·73
XII	,,	,,	,,	1·46	1·40	1·34	1·25	1·20	1·13	1·04	0·97	0·91	0·83	0·78
XIII	1450°C	,,	,,	1·41	1·36	1·30	1·24	1·20	1·15	1·08	1·03	0·97	0·93	0·87
XIV	,,	,,	,,	1·28	1·23	1·18	1·14	1·08	1·02	0·98	0·93	0·88	0·83	0·78
				0	40	80	120	160	200					
XV	1650°C	Pure argon	,,	1·40	1·34	1·30	1·25	1·19	1·16					
XVI	1600°C	,,	,,	1·63	1·59	1·55	1·50	1·47	1·43					
XVII	1550°C	,,	,,	1·37	1·33	1·29	1·26	1·22	1·19					
XVIII	1500°C	,,	,,	1·57	1·54	1·50	1·47	1·45	1·41					



2 *Showing variation of carbon concentration in bath with time for three iypical melts.*



3 *Showing variation of log [%C] with time for two typical melts*

were studied at temperatures 1 450°C, 1 500°C, 1 550°C, 1 600°C, and 1 650°C, two each at each of these temperatures. In the third set four melts were studied for determining the crucible reaction rates at 1 500°C, 1 550°C, 1 600°C, and 1 650°C, using purified argon gas. For melts of the second and third sets the gas flow rate was maintained at the constant level of 1 litre per minute. Samples were taken out at intervals of 20, 10, and 40 minutes respectively for the three sets. The method employed was to insert a steel rod through the sample hole, dip it into the bath and immediately take the rod out. The metal chilled against the side of the rod was sufficient for chemical analysis of carbon. The chemical analyses of all the melts were carried out in a Strohlein type carbon analyser. The analyses and other details of the melts are shown in Table I.

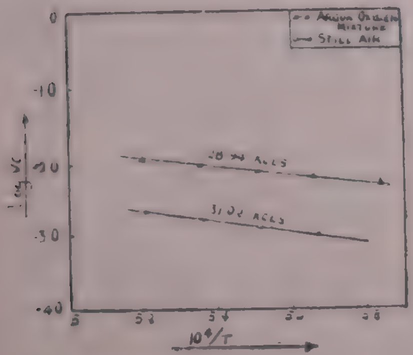
Experimental results and discussions

For all melts carbon concentration was plotted against time. In the high carbon ranges the curves were found to be straight lines showing constant rates of decarbonisation. At low carbon ranges the plots were non-linear showing their dependence on carbon concentrations. Typical concentration-time plots have been reproduced in Fig. 2, for three melts (Nos. II, VIII, and XVI). For two melts the experiments were carried down to sufficiently low values of carbon concentrations so that typical curved portions were obtained. The concentration at which departure from linearity occurs is identified as the critical carbon concentration range. The curved portions were replotted as log %C vs time as shown in Fig. 3 for the melts V and VIII. Replotted curves were straight lines indicating proportionality of carbon oxidation rates on carbon concentrations. From the straight line portions of the concentration-time plots (Fig. 2) the slopes were calculated and these gave for each case the gross values of carbon oxidation rate. The slopes of the last four melts (Nos. XV, XVI, XVII and XVIII) gave the values of the crucible reaction rates at different temperatures. These when deducted from the gross reaction rates for still air and argon-oxygen mixture gave the nett oxidation rates for different temperatures for the two gaseous media. The oxidation rates as obtained from the plots are reproduced in Table II.

The log rates (nett oxidation rates) were plotted against reciprocal absolute temperatures and from the slopes the apparent activation energies were determined. This is shown in Fig. 4 for the two gaseous media. It will be seen that the two values obtained are 28·94 kcal. for argon-oxygen mixture and 31·02 kcal for still air atmosphere. The true activation energy is determined from the rate constant of a reaction. In the

Gross and nett reaction rates for different gaseous media for different temperatures

Temp.	Crucible reaction rate % C/min	Vc in still air % C/min		Vc in 92% argon 8%O_2 mixture % C/min	
		Gross	Nett	Gross	Nett
1650°C	·0012	·0032	·0020	·0121	·0109
1600°C	·00095	·0028	·00185	·00997	·009
1550°C	·0009	·00215	·00125	·00805	·00715
1500°C	·0008	·0018	·0010	·0066	·0058
1450°C	·0007	—	—	·0052	·0045



4 *Showing variation of log Vc with reciprocal absolute temperature for both media*

present case it has been obtained from the nett oxidation rate. Though the factor of proportionality between the rate constant and the nett oxidation rate has been eliminated by taking the differences in the logs, it would be only proper to use the nomenclature 'apparent activation energy' for the present case.

The activation energy values obtained are slightly lower than the 34·6 kcal. obtained by K. Niwa Watanabe et al[4] in their laboratory melts. This is probably due to two reasons. Firstly, though experimenting with the same gaseous oxidising medium viz., 92% argon and 8% oxygen mixture K. Niwa Watanabe et al used a high frequency induction furnace for all their melts. In such a furnace the temperature is increased by increasing electrical input to the furnace. This causes an increased stirring of the bath, thereby increasing the oxidation rate. The ratios of the rates at any two temperatures of the difference in their log values are bound to be larger, thus increasing the slope of log rate-reciprocal temperature plots and the value of the activation energy. Secondly, K. Niwa Watanabe et al have assumed that the crucible reaction rate is constant and independent of temperature. This has been found to be otherwise (see Table II).

The apparent activation energy values obtained in the present investigation closely agree with those obtained by Vallet[5] from two sets of open hearth data of Fornander.[6] These are 27·5 kcal. and 29·0 kcal. The close proximity of the results of industrial open hearth and laboratory melts using two different gaseous media indicates that probably temperature affects the kinetics of carbon oxidation in the two cases similarly.

Conclusion

1. Presence of a critical carbon concentration has been observed.
2. Rate of oxidation of carbon at all concentrations above the critical concentration has been found to be independent of carbon concentration of the bath.
3. Rate of carbon oxidation at all concentrations lower than the critical concentration has been found to be proportional to the carbon concentration of the bath.
4. Temperature has a profound effect on the rate of carbon oxidation, the nett rate doubling itself in the temperature range investigated.
5. Crucible reaction rate is affected by temperature.
6. The apparent activation energies have been calculated to be 28·94 kcal for argon-oxygen mixture and 31·02 for still air.
7. The activation energy values compare favourably well with those obtained for industrial open hearth melts, indicating that temperature affects the kinetics of carbon oxidation in the two cases in a similar way.

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Notes and news

HOME NEWS

Iron ore deposits found in many parts of Kerala

Investigations by the State Geological Department have revealed the existence of large deposits of iron ore in various parts of Kozhikode district, according to the report of the department for 1964-65. The report said that prospecting operations conducted in six places in the district had revealed the existence of an estimated 15 million tonnes of iron ore deposits. An estimated 0·4 million tonnes of quartz magnetite with a low iron content had also been located in four places in Ernakulam district.

Source : Commerce, 4.12.65

Deposits of copper, zinc, iron ore and limestone in South Bhagalpur

Large deposits of copper, zinc, iron ore, limestone and beryl have been located in the hilly regions of South Bhagalpur district as a result of eight-month spot investigations conducted by the Geological Survey of India. Survey has again been taken up to ascertain the quality and area of expanse of the minerals secured.

Copper deposits have been detected in Baghmari village and beryl in Samukhia within Katoria police station. Besides, a good variety of fire clay has been detected in Kashri Hill, Bhadeshar Hill in Colgong Anchal and Tadwa Hill in Pirpainty Anchal.

Source : News Bulletin, Indian Press Service, 1.12,65.

Gold and silver in Sikkim

Traces of gold and silver have been discovered by recent I.B.M. exploration work in the Sikkim copper belt at Bhotang and Dikcher. Previous exploratory work in 1961 was done by G.S.I. India has extended financial and technical assistance to the Sikkim Mining Corporation which is in charge of the operations. The Sikkim Darbar holds 51% of the shares of the corporation while Government of India holds the remaining 49%.

Source : Coal and Steel. 1.12.1965

Rise in mineral production

The total value of mineral production in the country in the first seven months of 1965 registered 11% increase, according to the estimates prepared by the Indian Bureau of Mines.

The total value of minerals produced in the country till the end of July was Rs 1 376 million as against Rs 1 242 million in the corresponding period of the previous year. This excludes the value of petroleum, minor minerals and minerals declared as proscribed substances under the Atomic Energy Act, 1948. Quantitatively, the overall trend of mineral production during the month under review is reflected in the quantity index of mineral production (base 1960—100) which stood at 127·7 as against 142·1 in June this year.

Coal and lignite with an output of 5·65 million tonnes and 207 000 tonnes respectively, constituted the leading group. Next to coal and lignite, among the principal minerals in the ferrous group, the production of chromite was 1 613 tonnes, iron ore 1·33 million tonnes and manganese ore 124 000 tonnes. In the non-ferrous group, the production of bauxite was 49 326 tonnes, copper ore 38 532 tonnes, gold 323 kilograms, silver 401 kilograms, ilmenite 2 873 tonnes, lead concentrates 506 tonnes and zinc concentrates 866 tonnes. The output of principal non-metallic minerals was asbestos 309 tonnes, dolomite 76 526 tonnes, gypsum 92 000 tonnes, kyanite 3 637 tonnes, limestone 1·64 million tonnes, magnesite 20 125 tonnes, mica (crude) 1 902 tonnes and salt 344 000 tonnes.

Source : News Bulletin, Indian Press Service, 1.12.65

Pig iron plant for Bhavnagar

It is reported that a private party from Goa has decided to set up a pig iron plant in Bhavnagar in the Saurashtra region of Gujarat State. The plant may have an investment of Rs 3·75 crores, including foreign exchange worth Rs. 2 crores. It would employ nearly 700 people, and produce, 300 000 metric tons of foundry grade pig iron annually.

Source : Patriot, 2.12.1965

Special Cell in Steel Ministry

A 'Planning Cell' has been constituted in the Union Ministry of Steel and Mines to chalk out long-term plans for the development of steel and mining industries. It will work in co-operation with the Planning Commission, Hindustan Steel Ltd, Coal Development Corporation, the Mineral Development Corporation, the National Metallurgical Laboratory, Fuel Research Institute and other specialised organisations.

The Cell will concern itself more with long-term planning rather than with the 5-year plans or the annual plans. It will assess the range of price of coal in the coming decade or two so that the development is not inhibited either for want of necessary equipment or for want of capital. The Cell will also coordinate efforts of exploitation of different varieties of limestone so as to put the mining business to the best possible use. Among its other activities will be the improvement of technological know-how to help the Indian steel production to keep pace with the latest improvements in other countries.

Source : Hindu, 9.11.1965

Non-ferrous metals

The Steel and Mines Ministry is understood to have finalised a Rs 250-crore programme calculated to bring about a fourfold increase in the production of metals. A prominent feature of the plan is that projects, which were considered uneconomic in the past, will now be taken up. The programme, in the main, is to concentrate attention on the development of aluminium, copper, and zinc.

Aluminium

(i) Present estimated production of 68 000 tonnes is being increased to 273 000 tonnes at the end of 4th Plan.

(ii) Steps are being taken to expedite progress of schemes under implementation and by 1966-67 a production capacity of 113 000 tonnes is expected to be achieved. The Government has already undertaken the Korba and Koyna Projects in Public Sector: Technical consultancy of a German firm has been finalised for Koyna Project. Technical and financial assistance has been finalised with Hungary and USSR for Korba Project.

Hindustan Aluminium Corporation has been licensed to expand from 60 000 to 120 000 tonnes. Indian Aluminium Co. has been licensed to set up a new unit at Sharavathy (Mysore) for 30 000 tonnes. Work on these projects has advanced and is being accelerated.

(iii) Facilities for the manufacture of specialised products will be established at all manufacturing units, so that the aircraft industry, in so far as aluminium products are concerned, will be freed from imports.

Copper

(i) Indian Copper Corporation will expand their works from 9 600 to 16 500 tonnes. Development of new projects at Khetri, Rakha, Daribo and Kolihan will be undertaken. The construction of electrolytic refinery of Indian Copper Corporation Ltd. has been completed. Plans are underway for the primary stage of expansion of mine ore production and the installation of a flash smelter to treat the increased output of the ore.

(ii) Khetri Project which is designed to produce 21 600 tonnes of metal is already under implementation.

(iii) For Rakha Project, Soviet specialists are now in India to discuss and settle details of the Project.

(iv) Project Report by NMDC is under preparation for Daribo Project

(v) Preliminary work in Kolihan deposit has been intensified and is expected to be completed shortly.

Zinc

(i) The Government has recently decided to take over the Zawar mine of the Metal Corporation of India for undertaking the production of the metal in view of the importance of zinc metal for defence. The Project is now expected to be completed shortly and a provision of Rs 20 crores in the 4th Plan is contemplated for expanding the capacity of the unit.

(ii) The contract for setting up a Project to produce zinc from imported concentrates at Visakhapatnam with technical assistance from Poland is expected to be signed shortly.

Source : Economic Times, 14.10.1965.

OVERSEAS DIARY

High purity iron

Yawata's Tokyo Research Institute has succeeded in producing the purest form of iron ever developed through the application of an organic process as compared to the inorganic methods hitherto used in reducing impurities in iron. In the new process, which represents a completely new approach to the problem, the Institute has succeeded in producing iron with less than one tenth of the amount of impurities contained in what has hitherto been considered the purest iron.

Source: Yawata News, August 1965.

New moulding technique

The major disadvantage of the 'carbon dioxide' method of making moulds and cores for metal foundry use—the fact that under the heat of the molten metal they set rock hard and are difficult to remove from the casting—has been overcome by a new breakdown agent developed by the British Non-Ferrous Metals Association and marketed by two British firms—Foseco International Ltd and The Distillers Co. Ltd. The CO_2 core process has not made the headway expected, however, because no suitable breakdown agent has been developed so far to enable the mould to be broken easily after casting.

The new agent is based on glucose, an ingredient which has been tried before but which has exhibited certain disadvantages. These have now been completely overcome, claims the Non-Ferrous Metals Research Association, and moulds incorporating the new agent will readily disintegrate after casting into individual sand grains which are suitable for re-use. Substantial savings in fettling time should be many times greater than the cost of the breakdown agent, it is said. In addition, its introduction could lead to greatly increased use of the more economical CO_2 method of mould-making.

Source : British Information Services, B 1139.

Basic oxygen process gains in record steel production

Steel production in basic oxygen furnaces is now accounting for nearly 16 per cent of all steel made in the United States, up from 11 per cent in 1964, on the basis of preliminary seven-month production figures issued by American Iron and Steel Institute. The Institute Report disclosed that production for July and the first seven months of 1965 set records—11 563 000 net tons of ingots and steel for castings in July and 82 178 362 tons for the January to July period. These tonnages are to be compared with 10 105 609 tons for July of last year and 71 419 597 tons for the first seven months of 1964, both former records. While overall steel production rose by 15·1 per cent in the seven months compared with the year ago period, output by basic oxygen furnaces soared 66·3 per cent to record 13 095 965 tons from the 7 877 139 tons produced in the first seven months of last year. In 1964, the basic oxygen process moved ahead of electric furnaces in steel tonnage produced with a total of 15 442 186 tons, ranking second to the open hearths which continue to account for the major share.

Source : Blast Furnace and Steel Plant. Vol. 53, No. 9, Sept. '65.

Pellet usage rises

American Iron and Steel Institute statistics show that 1964 was a record year for production and consumption of iron ore agglomerates in the United States. Total production of agglomerates in the year was 84·4 million tons compared with 74·1 million tons in 1963. Of this total, sinter accounted for 54·4 million tons and pellets for 29·3 million tons. Over the five-year period 1960 to 1964, sinter production rose by 21 per cent and pellet production by 93 per cent. Over the same period pellet usage, which includes some imported material, increased by 179 per cent.

Source : British Steel Maker, Vol. 31, No. 9, Sept. 1965.

Testing metals for hydrogen

The Cambridge Instrument Company, London, has incorporated a flow method originally suggested by the British Welding Research Association into a new hydrogen-in-metals analyser. This unit measures hydrogen occluded in metals by analysing the gas mixture produced when the hydrogen from a heated metallic specimen diffuses into a standard volume of argon. Results are shown as integrated readings on an indicator or a recorder calibrated from 0 to 1 and 0 to 5 per cent hydrogen in argon. Test times are about 15 minutes for a $\frac{1}{4}$ inch diameter specimen and some 30 minutes for $\frac{1}{2}$ inch test pieces. The equipment is made up on an electric furnace kept at 650°C. and a kathermometer, or thermal conductivity measuring unit, connected in operation in a closed loop filled with pure dry argon—circulating by connection. The specimen is dropped into the furnace and its hydrogen quickly diffuses into the stream of argon moving through the reading becomes steady. Gas valves are provided for flushing out and refilling with argon. Drying chambers are fitted and a thermocouple is installed for checking the furnace temperature. Accuracy of this relatively inexpensive equipment is claimed to be comparable to that of vacuum units.

Source : Commerce, 4. 12. 1965.

Electric spark method of soldering nobler metals

Much of the noise, disturbed radio reception and telephone conversation, is due to constantly changing contact resistances. The best way so far in use was to replace the silver or other metallic contacts with nobler metals—gold or platinum. This however is costlier by many times since no method was known to solder these noble metals on the tip of the contacts. The Scientific Research and Designing Institute in Sofia (Bulgaria) has developed an electric spark method of soldering noble metals by which gold or platinum can now easily be placed on contact tips. The amount of metal required is also much less. Whereas normally only 16 contacts could be made from a gram of gold, now the same quantity will be sufficient for making one thousand contacts.

Source : Invention Intelligence, November, 1965.

Japan to purchase Australian pellets

Seven Japanese steel firms recently signed two contracts for the long-term purchases of Australian pellets—one with the Hamersley Iron Pty. Ltd. for 16 000 000 tons of pellets over 16 years beginning in 1968, and the other with Cliffs Western Australian Mining Co. for 71 400 000 tons of pellets over 21 years beginning in 1969.

The pellets under the contract with Hamersley assay Fe 62% on the basis 62% guaranteed and cost 18·5 cents per each per cent of Fe content. The pellets under the contract with Cliffs Western Australian Mining assay basically Fe 63% and cost 19·1 cents per each per cent of Fe content.

Source : Far East Iron & Steel Trade Reports, September , 1965.

Statistics

Targets of capacity and production for metals, mining and machinery industries

Industry	1965-66 (Likely achievement)		1970-71	
	Capacity	Production	Capacity	Production
METALS				
1. Iron and steel				
(a) Steel ingots ('000 tonnes)	8 900	7 100	14 600	13 000
(b) Finished steel ('000 tonnes)	6 600	5 300	11 000	10 000
(c) Pig iron for sale ('000 tonnes)	1 200	1 200	3 200	3 200
2. Alloy, tool and stainless steel (finished) ('000 tonnes)	50	35	500	400
3. Aluminium ('000 tonnes)	73	80	263	260
MINING				
4. Iron ore (million tonnes)	—	22	—	56
5. Coal (million tonnes)	—	67	—	113
MACHINERY				
6. Metallurgical and other equipment ('000 tonnes)	30	15	100	60
7. Steel castings ('000 tonnes)	170	60	300	250
8. Coal and other mining machinery ('000 tonnes)	45	12·5	60	45

Source : Eastern Economist, 17.9.1965

Production and import of principal non-ferrous metals in India

Metals	Production in Jan-June, '65 ('000 tonnes)	Imports (including alloys) in Jan-June, '65 ('000 tonnes)	Value of imports in Rs crores
Aluminium	30·5	12·3	3·5
Antimony	00·4	1·1	0·3
Copper	4·5	25·9	14·8
Lead	1·6	18·0	3·1
Zinc	5·3	44·4	7·3
Nickel	—	1·4	1·1
Tin	—	2·3	4·0
Total	42·3	105·4	34·1

Source : Commerce, 25.9.1965

months compared with

BANDEL NUMBER

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